Coupling of Electronic and Nuclear Degrees of Freedom in Diatomic Molecules: A Quantum Defect Study.

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Coupling of electronic and nuclear degrees of freedom in diatomic molecules: A quantum defect study

Gao, Hong, Ph.D.

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COUPLING OF ELECTRONIC AND NUCLEAR DEGREES OF FREEDOM IN DIATOMIC MOLECULES: A QUANTUM DEFECT STUDY

A Dissertation

Submitted to the Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Physics and Astronomy

by

Hong Gao
B.S., Tsinghua University, 1982
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ABSTRACT

The coupling of electronic and nuclear degrees of freedom in electron scattering from a homonuclear diatomic molecule has been studied using the frame transformation method in conjunction with the multichannel quantum defect theory (MQDT). Exploration of non-adiabatic effects resulting from large electron-molecule distances, resonances, and dissociation shows that the interconversion of energy between electronic and nuclear motion takes place mainly in the vicinity of the molecular target where the outermost electron couples strongly to the nuclei. MQDT enables us to describe these effects based on a body-frame quantum defect function, which can be obtained either from a short-range ab initio calculation (using Born-Oppenheimer approximation) or by fitting to the experimental data. This function thus provides sufficient information to characterize wavefunctions in asymptotic regions where the electron-molecule system may decay into different fragments (either the electron leaves the target, or else the two nuclei dissociate). The frame transformation method serves as a vehicle to convert the body-frame scattering parameter into laboratory-frame observables. We discuss two types of frame transformation methods for describing rovibrational coupling in this work. An energy-independent frame transformation is shown to be accurate enough to describe processes when the collision time of the scattering electron is negligible compared to the typical time for nuclear motion (i.e., when the energy dependence of the quantum defect is weak). In order to describe resonances (where the electron can be temporarily captured by the molecular target), we formulate an energy-dependent frame transformation
which explicitly includes the energy dependence in the frame transformation without invoking any electron-molecule compound states. Finally, we make a preliminary study of processes involving competition between ionization and dissociation. Short-range rovibrational coupling is shown to govern such processes as well, for one class of molecular photoabsorption processes.
A molecular system has more degrees of freedom than an atom. In addition to electronic excitations, a molecule can be rotationally and vibrationally excited. Moreover it can dissociate into two atomic fragments. The coupling between electronic and nuclear degrees of freedom makes the description of molecular spectra and scattering processes complicated. But this coupling generates much more interesting phenomena and richer spectra.

The Born-Oppenheimer approximation[1] has long been known to be a powerful tool for molecular problems. Separation of electronic and nuclear motions is made possible by the large mass disparity (the nuclei are more than a thousand times heavier than the electrons). Since the interaction force between the electrons and the nuclei are of the same order of magnitude, an electron moves much faster than a nucleus. In other words, the electronic motion is more sensitive to the instantaneous positions of the nuclei than to their velocity.[2,3] Thus the electronic eigenenergies and eigenfunctions can be determined first with the nuclei held fixed in space. Then the clamped-nuclei electronic energies (which depend parametrically on the nuclear coordinates) provide potentials in which the nuclei vibrate and rotate. This adiabatic description of electronic and nuclear motion in molecular structure calculations has also been adopted in the description of molecular scattering processes. In electron-molecule scattering, for instance, the so-called "adiabatic-nuclei
approximation"[4,2] solves the scattering problem first at a fixed nuclear distance and orientation. The laboratory-frame scattering amplitude is then obtained by calculating matrix elements of the fixed-nuclei scattering amplitude between initial and final rovibrational states.

While it is generally rather successful, this approximation breaks down in many circumstances.[2] Typical examples where this method fails are in the description of (1) a Rydberg molecule (where one electron is highly excited) or a low-energy electron-molecule scattering (where a very slow electron is incident on a molecular target); (2) a resonant scattering process (where the incident electron can be temporarily trapped in the vicinity of the molecular target); (3) an excitation of high vibrational states, including dissociative processes; and (4) a scattering process dominated by strong anisotropic long-range force like the \( r^{-2} \) dipole potential in electron scattering from a polar molecule (where the outer electron exerts a torque on the molecular target even at large distances[5]).

The common feature in all of these failures of the Born-Oppenheimer approximation is that the time scale of electronic motion becomes comparable to that of the nuclei. In the first example, the near-threshold electron can be found far away from the remaining molecular core. This outer electron moves so slowly that it is able to see the remaining core vibrate and rotate. This class of large-\( r \) breakdown (arising from large electron-core distances) consists of the most common non-adiabatic effect in electron-molecule scattering.[6]

Resonant scattering[7] is another typical example. In this case, the collision time of the scattering electron becomes comparable to or even longer than the periods for nuclear rotation (\( > 10^{-12} \) sec) or vibration (\( > 10^{-14} \) sec).[2]
In principle, all non-Born-Oppenheimer effects can be accounted for by including adiabatic and non-adiabatic corrections through a perturbation type treatment. Those correction terms involve evaluations of electronic matrix elements such as $<\varphi_j^{(e)}|\partial^2\varphi_i^{(e)}/\partial R^2>$ (where $|\varphi_i^{(e)}>$ is the electronic eigenfunction, and $R$ is the internuclear distance for diatomic molecules). However, this conventional state-by-state treatment could be cumbersome in many applications. In a Rydberg molecule, for example, as the outer electron reaches the threshold, Rydberg series converging to different rovibrational thresholds of the core strongly overlap with each other, and the interaction becomes too complicated to be handled in a perturbative way.\[8\]

There have been many attempts to describe those non-adiabatic effects.\[2,3\] The close coupling method takes the lead to describe the effects resulting from large-$r$ or near threshold scattering, and also scattering from a polar molecule.\[9\] The laboratory-frame close coupling treatment expands the total wavefunction of the electron-core system in terms of the complete set of eigenstates of the molecular core, leading to a system of coupled integro-differential equations for the outer electron radial wavefunctions.\[2\] Various sophisticated approximations have been developed and combined into the treatment to describe complicated static, exchange, and polarization interactions.\[2\] Although in principle this is an exact treatment, a practical difficulty arises when solving these close coupling equations in the core region where the scattering electron strongly couples to the nuclei. Different types of $R$-matrix methods\[10,11,12\] have been developed to solve the inner region problem, taking advantage of the fact that all complications are confined within a finite region of space.
Fano realized that the interaction between the scattering electron and the remaining core appears to be quite different depending on the distance between the outer electron and the core. When the outer electron is close to the core (region A), the strong interaction tends to couple the angular momentum of the electron to the internuclear axis. The motion of this electron, like that of the target electrons, is more sensitive to the positions of the nuclei. In other words, the internuclear distance $R$ and the total electronic angular momentum component $\Lambda$ along internuclear axis are well defined and approximately constants of the motion. The Born-Oppenheimer description is thus well justified in this region of space. As the electron moves out of this region, its angular momentum becomes less and less coupled to the internuclear axis. Eventually, its motion can be regarded as decoupled from the rotations and vibrations of the remaining core. The angular momentum of the electron ($l$), the rotational angular momentum of the core ($N^+$), and the core vibrational state ($v^+$) become good quantum numbers. The laboratory-frame close coupling expansion becomes effective in this region (region B). By dividing the configuration space of the outer electron into different regions, the complexity of the problem is reduced. The scattering matrix and other experimental observables can be obtained by matching the outer region close-coupling solutions to the inner region Born-Oppenheimer solution at some suitably chosen radius. The body-frame scattering information is thus transformed into the laboratory-frame one.

Multichannel quantum defect theory (MQDT)[13,14] provides the most natural framework to introduce the idea of frame transformation. The
concept of the quantum defect was originally developed to describe atomic Rydberg spectra. The interaction of the Rydberg electron with the residual atomic core, however complicated, is characterized by a quantum defect $\mu_l$ in the Rydberg energy formula (in a.u.): $E_{nl} = -Z^2/2(n - \mu_l)^2$. The quantum defect thus measures the deviation of the interaction between the outer electron and the core from the interaction between the electron and a point charge.\[15\]

The quantum defect method extends this idea further to treat continuum states as well, thus providing a natural link between scattering states and bound states. All the complicated interaction (static and exchange interactions, for instance) between an outer electron and the remaining molecular core (or target) is confined within the reaction region ($r < r_0$) enclosing the molecular target ($r_0$ is usually several Bohr radii), see Fig. 1(a). When the electron is outside the reaction zone, it essentially moves in the local and approximately central long-range Coulomb field of the remaining core (or zero field for electron scattering from a neutral molecular target if polarization effects are negligible). All that the short-range interaction does is to contribute a phase shift $\delta$ or a quantum defect $\mu$ ($\mu$ is equal to $\delta$ divided by $\pi$) to the solution in the asymptotic region, as shown in Fig. 1(b). The phaseshift or quantum defect, containing information about the short-range interaction between the outer electron and the molecular core, is all one needs in the asymptotic region to determine scattering properties or the bound energy levels. Description of the electron motion in the outer region is usually simple since the radial solutions in a long-range central field are known analytically in most cases.\[15\]
Figure 1. (a) Schematic illustration of a molecule in a Rydberg state: an outer Rydberg electron (e) and the remaining molecular ion ($M^-$); (b) Radial wavefunction of an electron in a continuum state in the outer Coulomb region ($r > r_0$). Short-range interactions shift the wavefunction relative to the wavefunction in the pure Coulomb field.
An advantage of this method is that one has flexibility to use different representations of wavefunctions of the system in different regions of space according to the prevailing interaction in those regions.[6] The so-called eigenchannel representation (the short-range Hamiltonian of the system is roughly diagonal in this representation[14]) is more appropriate in the inner region because it treats the outer electron on an equal footing with all other core electrons. In the outer region, on the other hand, a fragmentation channel (or close-coupling) representation (expansion of wavefunctions in terms of complete target states) is desirable since the electron is well separated from the remaining target. With the help of the Born-Oppenheimer approximation, the inner region problem can be solved like most molecular structure calculations. The resulting Born-Oppenheimer eigensolutions contain all the scattering information in the body-frame. This body-frame scattering information can later be transformed into the laboratory-frame by frame transformation methods.

Multichannel effects result from the fact that the remaining molecular target can be left in an excited state (electronically, and rovibrationally) after an electron collision. A fragmentation channel in MQDT is defined by specifying the complete set of quantum numbers of target energy eigenstates (electronic, rotational, and vibrational quanta, for instance) and the angular momentum quantum number of the outer electron.[8] Thus a whole Rydberg series of levels converging to a definite target eigenstate (ionic threshold) and the joining continuum above the threshold, comprise a single channel with the total energy as a running variable. Instead of considering the perturbation between different states, MQDT treats interactions between different
channels, thus giving a global description of complicated interaction in the system.

Fig. 2 shows schematically the interconversion of electronic and nuclear energies due to the coupling of the two degrees of freedom. Figure 2(a) shows two Rydberg series of \( \text{H}_2 \) converging to two different rotational states of the \( \text{H}_2^+ \) core. The levels near the threshold regions are very dense, and the two series overlap strongly. Channel interactions are expected to be strong in this region. A higher energy Rydberg electron in a state belonging to the series converging to \( N^+ = 2 \) rotational state of \( \text{H}_2^+ \) can collide with the core, take up the target rotational energy, and escape with \( \text{H}_2^+ \) left in the \( N^+ = 0 \) state (rotational preionization). Similarly, in Fig. 2(b) \( \text{H}_2 \) in high Rydberg states (the lowest two potential curves) can give up some of its vibrational energy to the Rydberg electron (vibrational preionization). These two examples exemplify how two channels converging to two different rovibrational thresholds of the target may interact with each other through short-range electronic-nuclear coupling (rovibrational coupling), interconverting energy between electronic and nuclear degrees of freedom. Jungen and coworkers\[8,16\] have successfully applied MQDT and the rovibrational frame transformation method to calculate the Rydberg states and photoabsorption processes of \( \text{H}_2 \). The rovibrational coupling has been shown to derive purely from the body-frame quantum defect function \( \mu_A(R) \), namely its \( R \) and \( \Lambda \) dependences. Fig. 3 shows the rovibrational levels of \( \text{H}_2 \) (\( J = 1 \)) in the \( C \ (2p\pi) \) state, taking into account the rovibrational coupling.\[8\] The large-\( r \) breakdown of the adiabatic approximation in those Rydberg levels has been accounted for by the rovibrational frame transformation in conjunction with
Figure 2. Schematic illustration of rovibrational preionization and predissociation in H$_2$. (a) Rotational preionization; (b) Vibrational Preionization; and (c) Predissociation.
Figure 3. Deviations of the rovibrational energy levels ($J = 1$) of H$_2$ (•) and D$_2$ (○) in C (2pπ) state calculated using QDT and using Born-Oppenheimer approximation, from Ref. [8].
MQDT. The improvement over the more usual Born-Oppenheimer treatment is substantial.

Also shown in Fig. 2(c) is a predissociation process of H$_2$. The excited electronic state of H$_2$ (3p$\pi$) can predissociate through electronic state 3p$\sigma$ (rotational coupling) converging to lower dissociation threshold. Interchange of energy between the electronic and nuclear degrees of freedom, in this case, takes place in the opposite sense.[16] A high Rydberg electron gives up some of its energy to nuclear motion. A dissociation process can be viewed as a high vibrational excitation. In our example, the dissociative state is a continuum vibrational level of the 3p$\sigma$ electronic state. Although the system usually dissociates along well-defined Born-Oppenheimer potential curves at large nuclear separations, the initial dissociation process at small $R$ is rather complicated. One expect non-adiabatic coupling between different states due to large nuclear velocity. Jungen proposed an eigenchannel $R$-matrix method to give a unified treatment of ionization and dissociation.[17] Based on this treatment, the above predissociation process can be described in terms of rovibrational coupling between different electronic states. Moreover, this method has been successfully used to explain how the ionization and dissociation compete in H$_2$ photoabsorption.[18] The body-frame quantum defect $\mu_A(R)$ was once again shown to provide sufficient information about the short-range electronic-nuclear coupling to describe even these dissociative processes. As well as being caused by rovibrational interactions, a dissociative process can also stem from electronic interactions between different electronic states. Giusti[19] formulated a perturbative method, combined with the $\text{rame}$ transformation method for rovibrational coupling, to account
for the dissociative process when the electronic coupling between the different electronic channels is weak.\[20\]

Apart from the aforementioned effects, there is also a class of nonadiabatic effects resulting typically from resonant scattering processes. It has also attracted much theoretical interests. In low energy electron-molecule scattering shape resonance, for instance, the centrifugal, polarization, and exchange forces may combine to form an attractive electron potential with a barrier.\[7\] An incident electron can thus be trapped in the vicinity of the molecular target for a period of time comparable to the period of the nuclear vibration. This common effect in low energy electron-molecule scattering manifests itself in a strong energy dependence in the scattering phase shift (or quantum defect).\[21\] According to Wigner, this energy dependence translates into a significant collision time delay: \( \tau_{\text{coll}} = 2\hbar \partial \mu / \partial \epsilon \) of the scattering electron in the reaction zone.\[22\] Besides resonant phenomena, a nonresonant electron scattering from a neutral target near threshold also falls into this category.\[21,23\] Results for \( \text{H}_2 \) obtained by Jungen and others\[8,16,25\] suggest that the rovibrational frame transformation method described above is virtually exact whenever \( \mu \) is independent of \( \epsilon \).\[21,23\]

There have been extensive theoretical treatments of such resonance phenomena. Nesbet proposed an "energy-modified adiabatic nuclei approximation" method to extend the validity of the conventional adiabatic nuclei approximation.\[26\] In his treatment, the scattering electron energy is included in the adiabatic electronic wavefunctions as a parameter. Thus different electronic channel energies are used in evaluating vibrational matrix elements of the scattering operator. Most theoretical treatments of resonances in

Greene and Jungen proposed, in the context of MQDT, an energy-dependent vibrational frame transformation method[21] which explicitly includes the energy dependence of the quantum defect in the frame transformation. This formulation defines a new type of real and local molecular compound potential for each eigenchannel, $\epsilon(\tau)(R)$, characterized by an $R$-independent electronic eigenphase parameter $\tau$ giving the phases of electronic eigenstates at the reaction zone surface. These potential curves are determined solely by the body-frame quantum defect function $\mu(\epsilon, R)$ generally provided either by \textit{ab initio} theory[32,33,34,35] or empirical data. Motion along this potential energy curve can then be treated in almost all cases within the Born-Oppenheimer approximation, which is typically valid whenever the outmost electron of the molecular complex moves within $r \leq r_0$. The failure of the Born-Oppenheimer approximation at large electronic distances is then fully accounted for by the quantum defect method.

The aim of this dissertation is to use the multichannel quantum defect theory and frame transformation method to study the coupling of electronic and nuclear degrees of freedom in homonuclear diatomic molecules.
We explore the non-adiabatic effects resulting from large electron-core distances, resonances, including dissociative processes. The long-range breakdown of the Born-Oppenheimer approximation which arises in electron scattering from a polar molecule is excluded. We direct our main efforts to the description of the electronic-nuclear coupling in resonance (strong energy dependence of quantum defect) and dissociative processes. Previous theoretical treatments of Greene-Jungen (energy-dependent vibrational frame transformation[21,23]) and Jungen (eigenchannel R-matrix method to treat ionization and dissociation[17,14]) have been reformulated so that the main complication involved in those methods — the iteration procedure — is avoided to give a simpler and more economical description. In our new rovibrational frame transformation approach,[36] for instance, molecular complex potentials are not explicitly introduced. We identify a special set of short-range Born-Oppenheimer eigenstates of the electron-target system, whose nuclear vibrational wave functions coincide with those of the unperturbed target. As a result, we find that the complicated short-range interaction between the scattering electron and the molecular target is fully included in the electronic wave functions, or more specifically in the body-frame electronic quantum defect function $\mu_A(\epsilon, R)$ (through its dependences on both the nuclear coordinate $R$ and electronic energy $\epsilon$). Effects of the energy dependence of short-range scattering parameters such as $\mu(\epsilon, R)$ can thereby be included in the frame transformation in a very simple way.

The outline of this dissertation is as follows. In Chapter 2 below, we give a complete quantum defect description of rovibrational couplings, and introduce the frame transformation concept. These elements form the
primary theoretical framework of this work. An application of this method to calculate vibrational energy levels of the ground electronic state of the hydrogen molecular ion follows.[37] Chapter 3 is devoted to the energy-dependent vibrational frame transformation method of Greene and Jungen. We present an $R$-matrix reformulation of this method and demonstrate through a simplified model calculation the importance of including the energy dependence of short-range scattering parameters in the frame transformation.[23] In Chapter 4 we present our alternative formulation of the energy-dependent rovibrational frame transformation method.[36] Comparison with the Greene-Jungen method is made in a calculation of the vibrational excitation of $N_2$ by electron collision. We then apply this method to study vibrational excitations of $H_2$ by electron impact. Finally, in Chapter 5 we show our preliminary study of competing ionization and dissociation processes using a noniterative eigenchannel $R$-matrix approach. Applications have been made in two test calculations of predissociation and ionization of $H_2$. 
As we mentioned earlier, MQDT by itself does not deal with solving the short-range problem. We will show below and in later chapters that a body-frame quantum defect function contains enough information about the short-range interaction to describe fully the wavefunction in the asymptotic region. In this chapter, we first summarize the MQDT formulation[8,14,23] for pure rovibrational interactions arising in electron collisions with a non-polar, N-electron diatomic molecule. This formulation also applies to Rydberg states of a neutral molecule. Thus an outer electron in the following context means either a scattering electron or a bound (or autoionizing) Rydberg electron. An application to calculate vibrational energy levels of the non-Rydberg molecule H$_2^+$ and its isotopes then follows.[37]

2.1 MQDT For Rovibrational Couplings: Asymptotic Behaviour

When the outer electron is sufficiently far from the molecular target, its motion is decoupled from the remaining core except for moving in the local, long-range field of the core. The angular momenta of the target ($N^+$) and of the electron ($l$) are approximately conserved.[6] The wavefunction of the system can be expanded in terms of the complete set of eigenstates of the
target, including the angular wavefunction of the escaping electron:[14]

$$\Psi_{\nu} = A r^{-1} \sum_i \phi_i(\omega) [f_i(r) \delta_{i\nu} - g_i(r) K_{i\nu}], \quad r > r_0,$$

(2.1)

with the channel expansion function $\phi_i(\omega)$ given by

$$\phi_i(\omega) = \varphi_{\omega_0}^{(s)}(N) \frac{\chi_i(R)}{R} \Phi_{J_M}^{(N^+)}(\hat{r}, \hat{R}).$$

(2.2)

Here $\varphi_{\omega_0}^{(s)}(N)$ is the target $N$-electron ground state wavefunction in $\Lambda_0$ state, $\chi_i(R)/R$ is the rovibrational wavefunction in this electronic state ($i = N^+, \nu^+$ indicates rotational and vibrational quantum numbers). $\Phi_{J_M}^{(N^+)}(\hat{r}, \hat{R})$ is an eigenfunction of the total angular momentum operators of the electron-core system $\hat{J}^2$ and $J_z$, and also the angular momentum operator of the remaining core $\tilde{N}^+2$ (and the angular momentum operator of the outer electron $\tilde{J}^2$). This eigenfunction is formed by coupling the angular momentum state of the scattering electron $Y_{lm}(\theta, \varphi)$ to the target rotational angular momentum state $Y_{N^+M-m}(\theta, \phi)$ in laboratory-frame:[6]

$$\Phi_{J_M}^{(N^+)}(\hat{r}, \hat{R}) = \sum_m Y_{lm}(\theta, \varphi) Y_{N^+M-m}(\theta, \phi) (lm, N^+M - m|lN^+JM),$$

(2.3)

where $(lm, N^+M - m|lN^+JM)$ is a Clebsch-Gordan coefficient. $Y_{lm}(\theta, \varphi)$ and $Y_{N^+M-m}(\theta, \phi)$ are spherical harmonic functions with $(\theta, \varphi)$ and $(\theta, \phi)$ denoting angles of electron and nuclei (internuclear axis) in laboratory-frame. Spin effects are ignored here, so we suppress the spin coordinates in the formulation. Thus $\omega$ contains coordinates of all degrees of freedom of the system except the radial coordinate of the outer electron.[14] The radial motion of the scattering electron is described by the regular and irregular functions $(f_i, g_i)$ evaluated at channel energy $\epsilon_i = E - E_i$ ($E_i$ is the eigenenergy of the molecular core) and orbital angular momentum $l$ in the long range field
of the molecular target. The \((f_i, g_i)\) are simply spherical Bessel functions in an electron-neutral scattering (zero-field approximation),\([23,21]\) and Coulomb functions in an electron-ion system.\([13,14]\) In what follows, we assume that only one angular momentum partial wave of the outer electron is dominant in the asymptotic region. A more general formulation including \(l\) coupling in the asymptotic region can be found elsewhere\([38]\) (and also in Chapter 4). \(A\) is the antisymmetrization operator. The reaction matrix \(K_{i,i'}\) contains all the short-range interaction information between the scattering electron and the core, and is directly related to the scattering matrix which can be measured by experiment. Since it is determined by short-range interactions, this real and symmetric \(K\) matrix is generally a smooth function of the energy \(E\).\([14]\)

It is worth mentioning again at this point that MQDT describes the coupling between the outer electron and the core through channel interactions instead of state-by-state interactions. In the above equation, the subscript \(i\) is the fragmentation channel index while \(i'\) labels alternative independent solutions of the Schrödinger equation in the asymptotic region.\([14]\) In each fragmentation channel, the total energy of the system \(E\) is regarded as a continuous variable in the expansion (2.1). In other words, the boundary conditions at infinity for the radial wavefunctions of the outer electron have not yet been imposed (wavefunctions in the closed channels accordingly have exponentially increasing components).\([14]\) Thus at this stage, the Rydberg states and the scattering states are treated equally. This is an advantage of the MQDT treatment. Both continuous and bound states have similar short range behaviour since the strong interactions prevalent in this region make the wavefunctions insensitive to a small change of energy from below threshold.
The qualitatively different behavior of wavefunctions for a continuum state (oscillatory) as opposed to a bound state (exponentially decaying) only emerge at large distances where physical boundary conditions are imposed.

Equation (2.1) above gives the reaction matrix representation of the independent solutions at a total scattering energy $E$. It is equivalent to writing the independent solutions in an eigenchannel representation, in which the reaction matrix is diagonal:

$$\psi_\alpha = Ar^{-1} \sum \phi_i(\omega)U_{i\alpha}[f_i \cos \pi \mu_\alpha - g_i \sin \pi \mu_\alpha], \quad r > r_0, \quad (2.4)$$

where $U_{i\alpha}$ and $\tan \pi \mu_\alpha$ are eigenvectors and eigenvalues of the $K$ matrix, respectively. In the eigenchannel representation, each eigensolution $\psi_\alpha$ has a common phase shift $\pi \mu_\alpha$ in all fragmentation channels $i$.

In standard MQDT procedures, a physically allowed solution of the Schrödinger equation is finally formed by superposing all independent solutions in Eq. (2.4):

$$\psi = \sum \psi_\alpha A_\alpha, \quad (2.5)$$

with $A_\alpha$ suitably chosen to satisfy boundary conditions at $r \to \infty$. For electron scattering by a neutral target with negligible polarizability, two independent radial solutions for the outer electron can be written as

$$f_i^0 = (2/\pi)^{1/2} k_i^{-i} r j_i(k_i r), \quad (2.6)$$

$$g_i^0 = (2/\pi)^{1/2} k_i^{i+1} r n_i(k_i r). \quad (2.7)$$

The above base pair is analytic in energy and should be used in case of zero long-range field. In this way the nonanalyticity of the energy-normalized
basis functions \((f_i, g_i)\) in energy at threshold can be eliminated, or in any case parametrized explicitly\([22,21,23]\). These two base pairs are related to each other by the relations \(f_i = k_i^{l+1/2} f_i^0, g_i = k_i^{-l-1/2} g_i^0\). In Eqs. (2.6) and (2.7), \(j_i(k_i r)\) and \(n_i(k_i r)\) are regular and irregular spherical Bessel functions and \(k_i = (2\epsilon_i)^{1/2}\) is the electronic wave vector. When closed channels \((\epsilon < 0)\) are involved, \(k_i\) is replaced by \(i\kappa_i\) with \(\kappa_i\) real and positive, but \((f_i^0, g_i^0)\) remain real. The asymptotic forms of \((f_i^0, g_i^0)\) for orbital angular momentum \(l\) are:

\[
\begin{align*}
f_i^0(r) &\to (2/\pi)^{1/2} k_i^{-l-1} \sin(k_i r - l\pi/2), \\g_i^0(r) &\to -(2/\pi)^{1/2} k_i^l \cos(k_i r - l\pi/2),
\end{align*}
\]

for \(\epsilon_i > 0\) (open channels) and

\[
\begin{align*}
f_i^0(r) &\to \kappa_i^{-l-1}[e^{\kappa_i r} - (-1)^l e^{-\kappa_i r}]/(2\pi)^{1/2}, \\
g_i^0(r) &\to -\kappa_i^{l}[(-1)^l e^{\kappa_i r} + e^{-\kappa_i r}]/(2\pi)^{1/2},
\end{align*}
\]

for \(\epsilon_i < 0\) (closed channels).

For an energy at which all channels are closed \((\epsilon \in Q, \epsilon_i < 0)\), the wavefunction component in each channel is required to decay exponentially, i.e.,

\[
\sum_a A_a U_{ia} [\kappa_i^{-l-1} \cos \pi \mu_a + \kappa_i^{l}(-1)^l \sin \pi \mu_a] = 0 \quad (i \in Q).
\]

The bound energy levels are found by solving the following determinental equation:

\[
\det|U_{ia} [\kappa_i^{-l-1} \cos \pi \mu_a + \kappa_i^{l}(-1)^l \sin \pi \mu_a]| = 0.
\]

Usually for any given total energy both open and closed channels are present. For closed channels, the above Eq. (2.12) applies. For open channels
(i ∈ P, εi > 0), we impose an outgoing wave boundary condition,\[22\] i.e., we require the asymptotic wavefunction to be written as a collision fragmentation channel form:

\[\Psi_i^{(+)} = A r^{-1} \sum_{i \in P} \phi_i(\omega) i^{-1} (2 \pi k_i)^{-1/2} \exp(i k_i r) S_{ii'} - \exp(-i k_i r) \delta_{ii'}, \quad r > r_0\] (2.14)

or equivalently in the collision eigenchannel form (in which \(S\) is diagonal)

\[\Psi_\rho = A r^{-1} \sum_{i \in P} \phi_i(\omega) T_{i \rho} (f_i \cos \delta_\rho - g_i \sin \delta_\rho), \quad r > r_0\] (2.15)

where \(S\) is the scattering matrix, \(\exp(2i \delta_\rho)\) and \(T_{i \rho}\) are eigenvalues and eigenvectors of the \(S\) matrix.

The boundary condition (2.15) can be implemented by requiring each open fragmentation channel \((i)\) in Eq. (2.5) to have a common collision eigenphase shift \(\delta_\rho\):

\[\sum_a A_a U_{i a} k_i^{l-1/2} \cos \pi \mu_a = T_i \cos \delta_\rho \quad (i \in P)\]
\[\sum_a A_a U_{i a} k_i^{l+1/2} \sin \pi \mu_a = T_i \sin \delta_\rho \quad (i \in P).\] (2.16)

Equations (2.12) and (2.16) can be written in a more compact form as a generalized eigenvalue problem:\[14\]

\[\Gamma \tilde{A} = \tan \delta \Lambda \tilde{A},\] (2.17)

with

\[\Gamma_{ia} = \begin{cases} U_{ia} \kappa_i^{l-1} \cos \pi \mu_a + \kappa_i^{l} (-1)^l \sin \pi \mu_a, & (i \in Q) \\
U_{ia} k_i^{l+1/2} \sin \pi \mu_a & (i \in P)\end{cases}\] (2.18)

\[\Lambda_{ia} = \begin{cases} 0 & (i \in Q) \\
U_{ia} k_i^{l-1/2} \cos \pi \mu_a & (i \in P)\end{cases}\] (2.19)
For $N_0$ open channels, Eq. (2.17) has $N_0$ nontrivial solutions, which yield $N_0$ values of the "collision eigenphase shift" $\delta_\rho(E)$, and $N_0$ corresponding column vectors of superposition coefficients $A_{a\rho}(E)$. Closed channels are "eliminated" through this procedure, but their effects have been built into $\delta_\rho(E)$. Thus the resulting "physical" phasshifts $\delta_\rho(E)$ and amplitudes $A_{a\rho}(E)$ usually acquire a strong energy dependence which will be eventually reflected in the final cross section as resonances. Autoionization resonances are typical examples where states belonging to a closed channel will decay through their interaction with open channels. The position and width of an autoionizing state can be determined from the eigenphase sum which usually shows a Breit-Wigner profile as a function of the energy near the resonance.

The eigenvectors of the $S$ matrix can be formed as follows:

$$T_{i\rho} = \sum_a A_{a\rho}[\Lambda_{ia} \cos \delta_\rho + \Gamma_{ia} \sin \delta_\rho], \quad (i \in P) \quad (2.20)$$

with $A_{a\rho}$ normalized such that $\sum_{i\in P} T^2_{i\rho} = 1$. The $S$ matrix is finally given in this case of zero long-range field by [14,23]

$$S_{i\nu} = \sum_{\rho} T_{i\rho} \exp(2i\delta_\rho) T_{\nu\rho}. \quad (2.21)$$

A similar expression can be found in Ref. [14] for the case of a long-range Coulomb field.

2.2 Rovibrational Frame Transformation

In the previous section, we summarized how MQDT describes the channel couplings in the asymptotic region. All the required information concerning rovibrational coupling is contained in the laboratory-frame reaction matrix $K$. This matrix can be obtained by connecting Eq. (2.4) to an accurate inner region solution, however it is obtained.
When the electron is inside the core region, its motion strongly couples to the molecular field. The Born-Oppenheimer approximation is well justified in this region. The inner region eigenstate can thus be written as

\[ \Psi_A = \varphi^{(e)}_A(N + 1)F(R)D^J_{AM}(\theta, \phi), \tag{2.22} \]

where \( \varphi^{(e)}_A(N + 1) \) is the \( (N + 1) \) electron wavefunction solved in the frame fixed on the nuclei. The total electronic angular momentum component along internuclear axis \( \Lambda \) is conserved in the inner region, to an excellent approximation. \( F(R) \) and \( D^J_{AM}(\theta, \phi) \) are nuclear vibrational and rotational wavefunctions, respectively. Here \( (\theta, \phi) \) are the Euler angles of the internuclear axis with respect to the frame fixed in space (the usual three Euler angles describing the orientation of an object in space reduce to two here for a linear molecule[39]). A symmetric rotor wavefunction \( D^J_{AM}(\theta, \phi) \) here is a good approximation for describing rotations of the molecule as a whole.[40,6]

When the electron just exits the core (but is still within the Born-Oppenheimer region), the above equation can be written as

\[ \Psi_A = A \varphi^{(e)}_{A_0}(N)F(R)X_{JM}^{(e)}(\hat{r}', \hat{R})[f \cos \pi \mu_A(R) - g \sin \pi \mu_A(R)], \quad r > r_0. \tag{2.23} \]

Here \( \varphi^{(e)}_{A_0}(N) \) is again the electronic wavefunction of the \( N \)-electron target ground state. \( X_{JM}^{(e)}(\hat{r}', \hat{R}) \) is the eigenfunction of the total angular momentum operators \( \hat{J}^2, J_z \) and of the electronic angular momentum component along the internuclear axis \( |\mathbf{L} \cdot \mathbf{R}| = \Lambda \). Different from \( \Phi^{(JN^+)}_{JM}(\hat{r}, \hat{R}) \), this eigenfunction is formed by coupling the angular momentum state of the outer electron in the body-frame \( Y_{IA}(\varphi', \varphi') \) (we assume here that the target molecule is in
a $\Sigma$ state, $\Lambda_0 = 0$. For more general cases, see Ref. [6], to $D^{(J)}_{\Lambda M}(\theta, \phi)$. In the case of a para-state of a diatomic molecule (antiparallel nuclear spins), Ref. [6] gives

$$X^{(J)}_{JM}(\vec{r}', \vec{R}) = |Y_\Lambda(\varphi', \varphi')D^{(J)}_{\Lambda M}(\theta, \phi) + Y_{-\Lambda}(\varphi', \varphi')D^{(J)}_{-\Lambda M}(\theta, \phi)| \left[ \frac{2J + 1}{8\pi(1 + \delta_{\Lambda 0})} \right]^{1/2}. \tag{2.24}$$

The body-frame quantum defect function $\mu_\Lambda(R)$ contains all the interaction information of the electron with the target in the body-frame. It can be obtained from ab initio calculations or else by fitting to the experimental data. In case of a Coulomb field (a similar expression holds for zero-field [22]), $\mu_\Lambda(R)$ can be extracted from the molecular Rydberg formula [8,14]

$$V_{n\Lambda}(R) = V_{\Lambda 0}(R) - \frac{Z^2}{2|n - \mu_\Lambda(R)|^2}. \tag{2.25}$$

Here $V_{n\Lambda}(R)$ and $V_{\Lambda 0}(R)$ respectively are potential energy curves of the neutral molecule and the molecular ion, and $Z$ is the electric charge of the remaining core.

Usually the energy dependence of the quantum defect, i.e., its dependence on the principal quantum number $n$, is weak, and can be neglected in many applications. The reaction matrix can thus be obtained by matching the laboratory-frame solutions Eq. (2.4) to the body-frame Born-Oppenheimer solutions Eq. (2.23) on the reaction zone surface, leading to an explicit formula for the reaction matrix,

$$K_{N^+ +, N^+ u^+} = \sum_\Lambda U^{(IJ)}_{N^+ \Lambda} < \chi_{N^+ u^+}(R) | \tan \pi \mu_\Lambda(R) | \chi_{N^+ u^+}(R) > U^{(IJ)}_{N^+ \Lambda}. \tag{2.26}$$

Here the rotational frame transformation matrix $U^{(IJ)}_{N^+ \Lambda}$ is a unitary matrix connecting the angular wavefunctions relevant in the body-frame [Hund's
coupling case (b)] and those relevant in the laboratory-frame [Hund's coupling case (d)]:[41,6,14]

\[ X_{JM}^{(l_A)} = \sum_{N^+} \Phi_{JM}^{(l_{N^+})} U_{N^+ A}^{(IJ)}, \]  

(2.27)

with \( U_{N^+ A}^{(IJ)} \) given by[6,14]

\[ U_{N^+ A}^{(IJ)} = (-1)^{J+\Lambda-N^+} [2/(1 + \delta_{A0})]^{1/2} (N^+0|I - \Lambda, J \Lambda) \]  

(2.28)

In obtaining the above equation, the energy dependence of the quantum defect function is totally neglected.[21,23] This in many cases serves as an excellent approximation. Since the electrostatic interaction is very strong near the core, the quantum defect \( \mu_A(R) \) and other short range interaction parameters are slowly varying functions of energy,[22] at least on the scale of rovibrational energy spacings.[8] This is especially true in high energy electron scattering where the electron crosses the target too rapidly for the target to be severely perturbed. Because the delay time is so short in these cases, the response of the target to the incident electron is not sensitive to its incident energy. However, we will show in the next Chapter that the above energy-independent frame transformation eventually breaks down, and the energy dependence of short-range quantities can play an important role in some processes.[21,23]

2.3 Vibrational Energy Spectra of \( \text{H}_2^+ \)

The above MQDT method has been applied to calculate vibrational energy levels of the 1σ\text{g} ground electronic state of the hydrogen molecular ion \( \text{H}_2^+ \) and its isotopes \( \text{HD}^+ \) and \( \text{D}_2^+ \). (This part of the work can be found in Ref. [37].) Like its atomic counterpart hydrogen, the hydrogen molecular ion is the simplest molecular system receiving extensive study both from
theory and experiment.[42,43,44] Theoretical calculations of rotational and vibrational states are greatly facilitated by the Born-Oppenheimer approximation. This separation of electronic and nuclear motions also provides the starting point for more accurate treatments, which include adiabatic and nonadiabatic effects accurately. A generalization of the Born-Oppenheimer picture to hyperspherical coordinates has been shown to give improved vibrational spectra for HD+,[45] as have numerous other formulations.[44] The purpose of this work is as follows. First of all, most previous MQDT treatments of molecular Rydberg spectra have involved a semiempirical element, in which small adjustments were made to the body-frame quantum defects \( \mu_A(R) \) so as to improve agreement with experiment. While these adjustments to \( ab\ initio \) data are typically small,[8] there remains the question of how far these MQDT analyses can be pushed to give a comprehensive \( ab\ initio \) theory. The simplicity of this system enables us to explore the validity of the MQDT and frame transformation from an \( ab\ initio \) point of view. For these systems the body-frame quantum defects \( \mu_A(R) \) can be calculated exactly. Secondly, the hydrogen molecular ion is a particularly unfavorable system for MQDT, as this treatment was designed to handle Rydberg states. Except for the ground state, all excited electronic states are either purely repulsive or else very weakly attractive at large internuclear distances, implying that nuclei simply dissociate following an electronic excitation. This system thus provides a critical test case for molecular MQDT. Lastly, the simplicity of this system also allows us to study such effects as energy dependence and finite nuclei mass on the quantum defect since they are all ignored in most treatments of molecular Rydberg spectra (\( H_2 \), for instance).
2.3.1 Description of the problem

The nonrelativistic Hamiltonian for \( H^+ \) can be written, in atomic units, as\(^{[44]}\)

\[
H = H_0 + H',
\]

where

\[
H_0 = -\frac{1}{2\mu_N} \nabla_R^2 - \frac{1}{2} \nabla_r^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R},
\]

\[
H' = -\frac{1}{8\mu_N} \nabla_r^2 - \frac{1}{2\mu_a} \nabla_R \cdot \nabla_r.
\]

Here \( r_A \) and \( r_B \) are the distances of the electron from nuclei \( A \) and \( B \) (with masses \( M_A \) and \( M_B \), respectively), \( R \) is the internuclear distance, \( \mu_N = M_A M_B / (M_A + M_B) \) is the reduced nuclear mass and \( \mu_a = M_A M_B / (M_A - M_B) \).

\(-\frac{1}{2} \nabla_r^2\) is the kinetic energy operator for the electron relative to the geometric center of the nuclei, and \(-\frac{1}{2\mu_N} \nabla_R^2\) is the nuclear kinetic energy operator.

The symmetry breaking term \(-\frac{1}{2\mu_a} \nabla_R \cdot \nabla_r\), which vanishes for \( H^+ \) and \( D^+ \), is neglected in our calculations of HD\(^+\) levels because this term, in the Born-Oppenheimer treatment, comes in only as a nonadiabatic correction. It mainly plays an important role near the dissociation limit, where the molecule can dissociate either to \( H + D^+ \) or \( D + H^+ \). The mass polarization term \(-\frac{1}{8\mu_N} \nabla_r^2\) makes a noneglimible contribution for hydrogen molecular ions. We neglect it here for simplicity, but show that it can be included exactly in a trivial way. This term contributes to the finite nuclear mass correction which is noticable in the light molecule like \( H^+ \), and negligible for other molecules.

In the calculation of vibrational levels of the \( H^+ \) ground electronic state \( 1s\sigma \), we only consider states having zero angular momentum, \( N = 0 \). Also we assume the electron to have purely \( s \)-wave character in the asymptotic
region. (Contributions from higher partial waves, *d*-waves for instance, can be neglected at the low energies considered here if one chooses a sufficiently large reaction zone radius.) The nuclei thus remain in their ground rotational state. When the electron is outside the reaction zone, the *α*th independent eigenchannel solution of the Schrödinger equation can be written as

$$\Psi_\alpha = \sum_{\nu^+} \chi_{\nu^+}(R) U_{\nu^+\alpha} [f_{\nu^+}(r) \cos \pi \mu_\alpha - g_{\nu^+}(r) \sin \pi \mu_\alpha], \ r > r_0. \quad (2.32)$$

Here the $\chi_{\nu^+}(R)$ are vibrational eigenstates of the core ($H_2^{++}$ in this case), quantized within a finite region $R_0 < R < R_f$. The validity of this box quantization is discussed below. The $(f_{\nu^+}, g_{\nu^+})$ are energy normalized ($Z = 2$) Coulomb functions\[13,14\] of the *s* electron evaluated at channel energy $\epsilon_{\nu^+} = E - E_{\nu^+}$ ($E$ and $E_{\nu^+}$ are energies of the molecule and the core, respectively). $U_{\nu^+\alpha}$ and $\tan \pi \mu_\alpha$ are the *α*th eigenvector and eigenvalue of the reaction matrix $K_{\nu^+\nu^+}$:

$$K_{\nu^+\nu^+} = \sum_\alpha U_{\nu^+\alpha} \tan \pi \mu_\alpha (U^T)_{\alpha \nu^+}, \quad (2.33)$$

with $T$ denoting the matrix transpose.

As in all MQDT calculations, the boundary conditions at $r \to \infty$ have not yet been imposed at this stage. ($\alpha$ labels the infinite number of independent solutions.) The $K$ matrix is thus a smooth function of energy. In many cases this energy dependence can be neglected in the energy range of interest so that the $K$ matrix can be calculated once and for all.\[14\] A physically acceptable solution of the Schrödinger equation is then formed by superposing all independent solutions in Eq. (2.32),

$$\Psi = \sum_\alpha A_\alpha \Psi_\alpha, \quad (2.34)$$
with the \( A_\alpha \) chosen such that \( \Psi \) obeys appropriate boundary conditions at infinity. Using the asymptotic form of \((f_{\nu^+}, g_{\nu^+})\), \([14]\) the bound Rydberg states of the molecule can be determined by solving the following algebraic equation:

\[
\sum \alpha A_\alpha U_{\nu^+\alpha} \sin \pi (\nu_{\nu^+} + \mu_\alpha) = 0. \tag{2.35}
\]

The allowed energy levels are accordingly those for which

\[
\det |U_{\nu^+\alpha} \sin \pi (\nu_{\nu^+} + \mu_\alpha)| = 0. \tag{2.36}
\]

In the above equations, \( \nu_{\nu^+} \) is the effective quantum number of the Rydberg electron in the \( \nu^+ \) channel, as given in Eqs. (2.39), (2.41), and (2.44) below.

Because the Born-Oppenheimer potential energy of the core is the repulsive Coulomb energy \( V^{(+)}(R) = 1/R \), the vibrational states of the core are purely continuous. In order to use the standard algebraic formulas of MQDT in the form of Eq. (2.35), we quantize the core states by confining the nuclei in a box, i.e., we require the nuclear wavefunctions to vanish at some given internuclear distances \( R_0 \) and \( R_f \). Figure 4 shows the Born-Oppenheimer potential curves of \( \text{H}_2^+ \) ground electronic state and \( \text{H}_2^{++} \) along with the quantized \( \text{H}_2^{++} \) vibrational states. The size of the box in \( R \) is chosen to be large enough so that the vibrational wavefunctions of hydrogen molecular ion for a range of levels \( \nu \leq \nu_{\text{max}} \) (\( \nu_{\text{max}} = 12 \) in this calculation) are exponentially small at the boundary, whereby this approximation introduces essentially no error. (It is possible, as in Ref. [17]'s, to allow the vibrational wavefunctions to extend beyond \( R = R_f \), by making an adiabatic treatment of the nuclear motion in that part of configuration space. For the present limited study it has not been necessary to do so.)
Figure 4. Potential energy curves of $\text{H}_2^+$ and $\text{H}_2^{++}$. $\text{H}_2^{++}$ "core" states are quantized by requiring the wavefunctions to vanish at $R_0$ and $R_f$. Here only those core states with $v^-$ even have been shown. The lowest vibrational state ($v = 0$) and highest state ($v = 12$) of $\text{H}_2^-$ in this calculation have also been shown.
The body-frame quantum defect $\mu_{n\ell\lambda}(R)$ can be obtained from the Born-Oppenheimer potential curve $V_{n\ell\lambda}(R)$ by the Rydberg formula Eq. (2.25). The set of lowercase quantum numbers $\{nI\ell\lambda\}$ is used to denote the Born-Oppenheimer electronic states of this single-electron molecule. Here $n$ is the principal quantum number, $I$ is the orbital angular momentum in the united atom limit and $\lambda$ is the projection of the orbital angular momentum along the internuclear axis of the molecule. In this calculation, the well-known $H_2^+1s\sigma_g$ Born-Oppenheimer potential curve[46] is used to extract the quantum defect $\mu_{1\sigma}$. Quantum defects $\{\mu_{n\sigma}, n = 1, 2, 3\}[42]$ are shown in figure 5, displaying the weak energy dependence of the quantum defect (i.e., the weak $n$-dependence of $\mu_{n\sigma}$) for the internuclear distances of interest in this calculation.

The laboratory-frame reaction matrix can be obtained in this case through a vibrational frame transformation:

$$K_{v'v''\sigma} = \int \chi_{v''}(R) \tan \pi \mu_{1\sigma}(R) \chi_{v'}(R) dR.$$  \hspace{1cm} (2.37)

The information contained in the $K$ matrix can be equivalently calculated from the quantum defect matrix[25]

$$\mu_{v'v''\sigma} = \int \chi_{v''}(R) \mu_{1\sigma}(R) \chi_{v'}(R) dR, \hspace{1cm} (2.38)$$

which is preferable to calculate numerically as the integrand has no singularities. [In the limit of an infinite vibrational basis, the eigenvectors of both Eq. (2.37) and Eq. (2.38) are $\chi_{v'}(R)$, while the eigenvalues of these two matrices are $\tan \pi \mu_{1\sigma}(R)$ and $\mu_{1\sigma}(R)$, respectively. We assume that for a truncated basis also, the eigenvectors $U_{v'\alpha}$ of $K_{v'v''\sigma}$ coincide with those of $\mu_{v'v''\sigma}$, with respective eigenvalues $\tan \pi \mu_{\alpha}$ and $\mu_{\alpha}$. It is seen from the above equations...
Figure 5. Quantum defect $\mu_{\text{neo}}(R)$ for $n = 1, 2, 3$. 
that this single body-frame quantum defect, which describes the complicated (fixed-nuclei) interaction between the electron and the nuclei, serves as the input for the quantum defect calculation.

2.3.2 Vibrational spectra of $H_2^+$ Effects associated with the portion of the Hamiltonian denoted $H'$ in Eq. (2.31), such as the change in the electron reduced mass, can be treated in a variety of ways, both in standard Born-Oppenheimer calculations and in MQDT calculations. To gain a better understanding of these alternatives, we have performed the calculations on $H_2^+$ at three different levels of sophistication described below.

(a). Total Neglect of $H'$

The conventional Born-Oppenheimer approximation is obtained by regarding the nuclei as infinitely massive in solving for the fixed-nuclei potential curve $V_{n\lambda}(R)$, the eigenvalue of $H_0$ in Eq. (2.30) with $\bar{R}$ held constant. The correct nuclear reduced mass $\mu_N$ is used of course when solving for the vibrational energy spectrum in the Born-Oppenheimer potential $V_{n\lambda}(R)$. The result of this standard calculation is the curve (1) in Fig. 6, plotted as the difference between each Born-Oppenheimer total energy level and the corresponding "exact" nonrelativistic theoretical energy levels from Ref. [47]. It is seen that neglect of the nuclear mass dependent terms in the electronic potential (i.e., the "strict" Born-Oppenheimer approximation) causes the vibrational energy levels to be nearly 60 cm$^{-1}$ too low. Interestingly, this error is roughly the difference in the energies of a ground state hydrogen atom calculated with finite or with infinite nuclear mass.

A quantum defect calculation is next carried out for $H_2^+$ as outlined above in Sec. 2.3.1, using $\mu_{1\omega}(R)$ in the integrals of Eq. (2.38) to determine
Figure 6. Difference between the calculated and exact vibrational energy levels, using either quantum defect theory (QDT) or else the Born-Oppenheimer approximation (BO) for $H_2^+$. Curves with open (filled) circles are the results with (or without) the mass polarization term. The curve with triangles is the QDT calculation including the finite nuclear mass effect only in the "outer region". The exact values are taken from Ref. [47].
the quantum defect matrix $\mu_{v^+,v^+}$. The $\mu_a$ used in Eq. (2.36) determining the MQDT energy levels are then the eigenvalues of this matrix while the orthogonal matrix $U_{v^+\alpha}$ is formed from the corresponding eigenvectors. Because we are totally neglecting $H'$, we calculate the effective quantum numbers $\nu_{v^+}$ in Eq. (2.36) using the true (i.e. not reduced) electron mass:

$$\nu_{v^+} = \frac{Z}{\sqrt{-2\varepsilon_{v^+}}}.$$  \hspace{1cm} (2.39)

The box size used for $H_2^+$ is defined by $R_0 = 0.5$ a.u., $R_f = 7.5$ a.u., which allows us to calculate vibrational levels with $v \leq 12$. All vibrational channels of $H_2^{++}$ were included from $v^+ = 0$ to $v^+ = 119$, resulting in an unusually large MQDT calculation, with 120 channels. Nevertheless the search for $H_2^+$ vibrational levels with $v \leq 12$ which satisfy Eq. (2.36) was accomplished in roughly 40 min of CPU time on a RIDGE 32C computer. (In fact the MQDT calculation can be transformed into a converged calculation using only 15 to 25 “effective channels” along the lines sketched in the appendix of Ref. [37])

The errors in the resulting MQDT energy levels obtained in this manner are shown as curve (2) in Fig.6. Clearly the resulting errors are very comparable to those obtained in the corresponding strict Born-Oppenheimer approximation neglecting $H'$, the MQDT results even showing a slight improvement over the Born-Oppenheimer results. We find it surprising that the MQDT frame transformation procedure is capable of describing the vibrational energy levels of the $H_2^+$ ground state, which is far more a “valence-type” molecular state (in conventional terminology) than a “Rydberg” state. The MQDT “picture” of $H_2^+$ as consisting of a Rydberg electron orbiting outside a vibrating $H_2^{++}$ core appears unsound initially, in view of the unstable
nature of this core, yet it produces results virtually equivalent to (in fact slightly better than) the well-established Born-Oppenheimer procedure.

It is also interesting to show, for pedagogical purposes, that the MQDT channel expansion gives results compatible with the Franck-Condon principle. The outer region wavefunction Eq. (2.34) is an expansion in terms of the core vibrational states. In Fig. 7 we show explicitly the channel probability amplitudes[48]

\[ z_{v^+}(E_v) = \nu_{v^+}^{3/2} \sum_{\alpha} A_{\alpha} U_{v^+\alpha} \cos \pi (\nu_{v^+} + \mu_{\alpha}), \]  

(with \( z_{v^+} \) normalized by \( \sum_{v^+} z_{v^+}^2 = 1 \)), in each channel \( v^+ \) at energies of \( H_2^+ \) \( v = 0 \) and \( v = 12 \) vibrational states. These results are indistinguishable from standard Franck-Condon overlap integrals connecting the vibrational states of \( H_2^+ \) to those of \( H_2^{++} \). It can be seen that the most dominant contribution to the wavefunction [Eq. (2.34)] comes from the Franck-Condon region. The number of channels \( v^+ \) is so large that \( z_{v^+} \) appears to be a continuous function, although it is in fact discrete.

(b). Partial Inclusion of Electron Reduced Mass Effects

In their MQDT calculation of \( H_2 \) bound levels, Jungen and Atabek[8] use the conventional Born-Oppenheimer approximation in the inner region and obtain a body-frame quantum defect \( \mu_A(R) \) independent of nuclear mass. In the outer region, the system is exactly described in terms of a rovibrational channel expansion in the laboratory-frame, in which the outermost electron sees a vibrating core with finite nuclear mass. Thus the effective quantum number \( \nu_{v^+} \) in Eq. (2.36) was calculated in Ref. [8] using the reduced electron
Figure 7. Comparison of the Franck-Condon overlap integral $< v^+, v >$ and the MQDT channel probability amplitude $z_{v'}$. The two curves are indistinguishable on the scale of the graph. (a) $H^+_0 (v = 0)$; (b) $H^+_1 (v = 12)$. 
mass $\mu_e = (1 + \frac{1}{4\mu_N})^{-1}$:

$$\nu_{v^+} = \frac{Z}{\sqrt{-2\epsilon_{v^+}/\mu_e}}, \quad (2.41)$$

where $\mu_N$ is half of the proton mass in the case of $H_2^+$. The errors in energy levels of $H_2^+$ obtained using this same method are plotted as curve (3) in Fig. 6. Apparently the incorporation of electron reduced mass effects improves upon the MQDT calculation described in method (a) above, though it appears to overcorrect to some extent.

The improvement of this result over the MQDT result with infinite nuclear mass [curve (2)] can be explained as follows. For a given effective quantum number $\nu_{v^+}$, each channel energy $\epsilon_{v^+}$ is directly proportional to the electron reduced mass $\mu_e$. Thus a change of $\Delta \mu_e$ in the reduced mass used in calculating $\nu_{v^+}$ in Eq. (2.41) produces a proportionate change in the channel energy, $\Delta \epsilon_{v^+} = \frac{\Delta \mu_e}{\mu_e} \epsilon_{v^+}$. When averaged over the channel probability amplitude [see Eq. (2.40)], the change in the final energy level is given by

$$\Delta E = \frac{\Delta \mu_e}{\mu_e} \sum_{v^+} z_{v^+}^2 \epsilon_{v^+}. \quad (2.42)$$

By direct numerical calculations, we have verified that the contribution given by Eq. (2.42) is equal to the difference between the curve (3) and the curve (2) in Fig. 6 (to within errors of approximately 0.1 cm$^{-1}$).

Inclusion of electron reduced mass effects in this approximate manner (in the "outer region") partially improves the results, but appears to overcorrect for this effect (i.e., the energy levels calculated in this way are higher than the "exact" levels). We will show in method (c) that the change in the electron reduced mass also affects the quantum defect, making an additional contribution to the vibrational levels. This reduced mass effect on the
"inner region" has opposite sign to that shown in Eq. (2.42), in the present example of the $H^+_2 1s\sigma$ state.

(c). Total Inclusion of Electron Reduced Mass Effects

As a matter of fact, the mass polarization term can be included in the calculation exactly (for a one-electron homonuclear molecule) by a trivial scaling transformation: $\tilde{r} \equiv \mu_e r$, $\tilde{R} \equiv \mu_e R$, and $\tilde{\mu}_N \equiv \mu_N / \mu_e$, with $\mu_e^{-1} = 1 + 1/4\mu_N$ ($\mu_e$ and $\mu_N$ are in units of electron mass), we have the following rescaled Hamiltonian in (a.u.):

$$\mathcal{H} \equiv \frac{\mathcal{H}}{\mu_e} = -\frac{1}{2\tilde{\mu}_N} \nabla^2_{\tilde{R}} - \frac{1}{2} \nabla^2_{\tilde{r}} - \frac{1}{\tilde{r}_A} - \frac{1}{\tilde{r}_B} + \frac{1}{\tilde{R}},$$

(2.43)

which has identical form to $\mathcal{H}_0$ in Eq. (2.30). The mass polarization term is thus apparently removed from the Hamiltonian although its effect is fully included.

When applying the Born-Oppenheimer approximation to this new Hamiltonian, we are able to calculate the vibrational spectrum of $H^+_2$ in the rescaled Born-Oppenheimer potential curve $\tilde{V}_{1s\sigma}(\tilde{R})$, which is formally identical to $V_{1s\sigma}(R)$. The rescaled reduced nuclear mass $\tilde{\mu}_N$ must then be used in solving the vibrational Schrödinger equation. Curve (4) in Fig. 6 shows the error in the resulting energy levels $E_v$, relating to the energy eigenvalue $\tilde{E}_v$ of the hamiltonian $\mathcal{H}$ by $E_v = \mu_e \tilde{E}_v$.

The corresponding MQDT calculations utilize the rescaled Born-Oppenheimer quantum defect $\tilde{\mu}_{1s\sigma}(\tilde{R})$, which is likewise formally identical to $\mu_{1s\sigma}(R)$, (i.e. the value of $\tilde{\mu}_{1s\sigma}$ at $\tilde{R} = 2$ coincides exactly with the value of $\mu_{1s\sigma}$ at $R = 2$). The vibrational levels of $H^+_2$ are solved just as in the method (a), except using rescaled energy, mass, and distance units. In the
final step of using MQDT to calculate the energy spectrum, the rescaled effective quantum number

\[ \tilde{\nu}_v = \frac{Z}{\sqrt{-2\epsilon_v}}. \]  

(2.44)
is used. Curve (5) in Fig. 6 shows the errors in \( \text{H}_2^+ \) vibrational levels obtained using this procedure.

Interestingly, this trivial incorporation of the mass polarization term in the conventional Born-Oppenheimer approximation shifts both MQDT and Born-Oppenheimer levels by the same amount relative to the corresponding infinite nuclear mass results (lowest two curves in Fig. 6). For the Born-Oppenheimer results [the curves (1) and (4)] this amount can be shown to be the improvement due to including the adiabatic correction term\[46\] \( \langle \phi| - \frac{1}{\hat{\mu}_N} \nabla^2 \rangle \phi \) in the Born-Oppenheimer potential. For the MQDT results [curves (2) and (5)], the improvement can be explained as follows. The electron reduced mass effect is taken into account not only in the outer region [see Eq. (2.41)], but also in the inner region. The rescaled quantum defect \( \tilde{\mu}_{1\infty}(\tilde{R}) \) contains the electron reduced mass effect. The difference between \( \mu_{1\infty}(R) \) (with real electron mass) and \( \tilde{\mu}_{1\infty}(\tilde{R}) \) (with reduced electron mass) is around \( \Delta \mu(R) \sim 10^{-5} \) at a given value of \( R \). The change in the body-frame electron energy due to the change in the electron mass can be written as

\[ \Delta \varepsilon(R) = -\Delta \mu_{\varepsilon_{1\infty}}(R) - \frac{\mu_{\varepsilon}}{Z} (-2\epsilon_{1\infty}(R))^{3/2} \Delta \mu(R). \]  

(2.45)

When averaged over \( R \), we have \( \Delta E = \Delta E_1 + \Delta E_2 \), where

\[ \Delta E_1 = \Delta \mu_{\varepsilon} \sum_{v^+ v^+} z_{v^+} z_{v^+} \int \chi_{v^+}(R) \epsilon_{1\infty}(R) \chi_{v^+}(R) dR, \]  

(2.46)

\[ \Delta E_2 = -\frac{\mu_{\varepsilon}}{Z} \sum_{v^+ v^+} z_{v^+} z_{v^+} \int \chi_{v^+}(R) [-2\epsilon_{1\infty}(R)]^{3/2} \Delta \mu(R) \chi_{v^+}(R) dR. \]  

(2.47)
\( \Delta E_1 \), which is the contribution from long range, is identical to Eq. (2.42) in our calculations, to within the accuracy of 0.01 cm\(^{-1}\). \( \Delta E_2 \) contains the contribution from short range, i.e., contributions due to the change in the quantum defect. This term, which makes a considerable contribution, is ignored in the formulation of Jungen and Atabek [see (b) above]. Since \( \Delta \mu(R) > 0 \), this term is opposite in sign to Eq. (2.46). Numerical calculation shows that the sum of \( \Delta E_1 \) and \( \Delta E_2 \) in Eqs. (2.46) and (2.47) explains quantitatively the improvement of these MQDT results in this part (c) over those in part (a), to an accuracy of 0.05 cm\(^{-1}\).

It can also be shown that the remaining error in the Born-Oppenheimer calculation [the difference of curve (4) from zero] can be almost entirely eliminated by further including the other part of adiabatic correction term \([46] < \phi| - \frac{1}{2\mu N} \nabla^2_R \phi > \) in the Born-Oppenheimer potential. It is worth mentioning that MQDT results [curves (2) and (5)] are slightly better than the corresponding Born-Oppenheimer results [curves (1) and (4)]. Instead of adopting the Born-Oppenheimer approximation in the whole configuration space, MQDT using the frame transformation adopts a laboratory-frame expansion in the outer region. This procedure describes the coupling between electronic and nuclear motions, essentially exactly in the large - \( \tau \) limit.

Apparently the remaining discrepancy of MQDT results [the difference of curve (5) from zero] is partly due to the remaining adiabatic correction at smaller distances and partly due to approximations used in the frame transformation. We will discuss these aspects in Sec. 2.3.4 below.
2.3.3 Vibrational spectra of HD\textsuperscript{+} and D\textsubscript{2}\textsuperscript{+} Method (c) in Sec. 2.3.2 has also been applied to calculate energy levels of HD\textsuperscript{+} and D\textsubscript{2}\textsuperscript{+}. As mentioned earlier, the asymmetric term in \( H' \), which is not important for the low lying vibrational states of HD\textsuperscript{+}, is neglected in the calculation for HD\textsuperscript{+}. The box sizes for HD\textsuperscript{+} and D\textsubscript{2}\textsuperscript{+} are \( \{ R_0 = 0.5 \text{ a.u., } R_f = 6.5 \text{ a.u.} \} \) and \( \{ R_0 = 0.5 \text{ a.u., } R_f = 6.0 \text{ a.u.} \} \), respectively. One hundred channels are included in the MQDT calculations for both. The errors of these calculations are shown in Fig. 8. As expected, both the Born-Oppenheimer and MQDT results improve as the nuclear mass increases from H\textsubscript{2}\textsuperscript{+} to D\textsubscript{2}\textsuperscript{+}.

2.3.4 Discussion Based purely on the H\textsubscript{2}\textsuperscript{+} 1s\sigma\textsubscript{g} potential curve, or the corresponding quantum defect \( \mu_{1s\sigma}(R) \), we are able to calculate the vibrational states of H\textsubscript{2}\textsuperscript{+} and its isotopes. MQDT adopts the molecular frame with the Born-Oppenheimer approximation only at short range where the electron moves in the strong nuclear field. Outside the reaction zone, the motion of the Rydberg electron is decoupled from that of the molecular core so that a laboratory-frame description is more adequate. Thus a class of non-Born-Oppenheimer effects resulting from large electron-core distances is accounted for by this method. The improvement, while modest for H\textsubscript{2}\textsuperscript{+}, is clearly shown in Figs. 6 and 8. A greater improvement is expected for true Rydberg molecules.

It is worth mentioning that these results of calculations are converged with respect to both the box size and the number of channels for all levels shown. This can be seen from the channel probability amplitude \( z_{v+} \) in Fig. 7. However, there is still a remaining systematic discrepancy (i.e.,
Figure 8. Difference between the calculated and exact vibrational energy levels, using either quantum defect theory (QDT) or else the Born-Oppenheimer approximation (BO) for HD$^+$ and D$_2^+$. The exact values are taken from Ref. [47].
the increasing errors as $v$ increases) between the MQDT results and "exact" calculations. This derives in part from the coupling between electronic and nuclear motions (primarily the adiabatic correction term $<\phi|-\frac{1}{2}\nabla_R^2|\phi>$) at small electron distances. This short range effect cannot be totally ignored for $H_2^+$. Aside from this small effect, the only other possible explanation for the residual errors in the MQDT calculation is its neglect of two types of energy dependences: that of the body-frame quantum defect, and that of the Coulomb functions (through the approximation $(f,g) \sim (f_{\nu},g_{\nu})$) used in this calculation.

The body-frame quantum defect is not only a function of internuclear distance, but also a function of the body-frame energy of the electron (i.e. a function of $n$ as shown in Fig. 5). This energy dependence is not strong in typical Rydberg spectra of neutral diatomics, and has been ignored in the usual vibrational frame transformation method. However, the energy dependence of the quantum defect plays an important role in resonant electron-molecule collisions. Figure 5 shows that, for the ns$\sigma$ states of $H_2^+$, $\partial\mu/\partial\epsilon$ (or $\Delta\mu(R)$ due to energy dependence) is negative. This will lead to a positive correction $\Delta\epsilon(R) = -[\epsilon_{1\sigma}(R)]^{3/2}\Delta\mu(R)/(Z\sqrt{\mu_e})$, i.e., an increase in the final vibrational energy levels. This energy dependence becomes stronger as the internuclear distance increases, and will give a larger correction to the higher vibrational states.

The neglect of the energy dependence of $(f,g)$ in the $K$-matrix formulation can be removed in principle by reformulating the frame transformation in terms of the $R$ matrix rather than the $K$ matrix, i.e., using the logarithmic derivative $\zeta(\epsilon, R)$ defect. One drawback of this reformulation
is that the energy dependence of \( \zeta \) is stronger than that of \( \mu \). We will discuss in the following chapters this class of non-adiabatic effect arising from the energy dependence of the quantum defect.
CHAPTER 3

ENERGY-DEPENDENT VIBRATIONAL FRAME TRANSFORMATION METHOD OF GREENE AND JUNGEN: A MODEL STUDY

In the previous chapter, we have discussed how the quantum defect method combined with an energy-independent rovibrational frame transformation can be used to describe a class of non-Born-Oppenheimer effects resulting when the outer electron is far from the remaining core. In these cases, a slow electron far from the core gets accelerated at short-range so that it crosses the core region too swiftly for the target to be disturbed. In other words, the nuclei are frozen when the scattering electron is inside the target. The quantum defect function is thus nearly energy-independent. However, it is quite common in low-energy electron-molecule scattering that the outer electron stays in the neighbourhood of the molecular target for a much longer time. In a resonant process, the incident electron can be trapped by the target molecule for a time comparable to the rotational or vibrational periods of the nuclear motion.[7,14] The long collision time of the scattering electron is reflected in the scattering phase shift (or quantum defect) as a strong energy dependence. This gives rise to a second class of nonadiabatic effects. Whenever the energy dependence becomes important, the energy-independent rovibrational frame transformation [see Eq. (2.26)] described in the previous chapter is questionable.
The strong energy dependence of the short-range scattering parameters brings in an additional difficulty to theoretical descriptions because of stronger correlations between the electronic and nuclear motions when the outer electron is inside the core. Greene and Jungen proposed a vibrational frame transformation method\cite{21} to incorporate the energy dependence of quantum defect in the frame transformation. Like most theoretical treatments of resonances, this method introduces a set of electron-molecule compound potential curves $V^{(\tau)}(R)$ each of which is defined as a sum of the target molecular potential energy $V_T(R)$ and electronic energy $\epsilon^{(\tau)}(R)$,

$$V^{(\tau)}(R) = V_T(R) + \epsilon^{(\tau)}(R).$$  \hspace{1cm} (3.1)

The electronic energy is extracted from the body-frame quantum defect by "inverting" the following equation:

$$\mu(\epsilon, R) = \tau.$$  \hspace{1cm} (3.2)

Here $\tau$ is an $R$-independent, and arbitrary, electronic phase parameter at this stage. All the complicated short-range electronic and nuclear interactions are contained in the quantum defect function $\mu(\epsilon, R)$, its $R$ and $\epsilon$ dependences. When the electron is inside the molecular target, the nuclei are allowed to move in this real, local potential curve of the complex $V^{(\tau)}(R)$, which incorporates the full dependence of the nuclear motion on the incident electron energy. It is then straightforward to solve the vibrational Schrödinger equation

$$-\frac{1}{2\mu_N} \frac{d^2}{dR^2} + V^{(\tau)}(R) - E^{(\tau)}|F^{(\tau)}(R) = 0$$  \hspace{1cm} (3.3)

for energy levels $E^{(\tau)}_\alpha$ and vibrational wavefunctions $F^{(\tau)}_\alpha(R)$. For an arbitrary $\tau$, $E^{(\tau)}_\alpha$ (which is also the energy of the system) is not generally equal to the
given total scattering energy $E$. At each energy $E$, an iteration procedure is used to select only those values of $\tau$ which yield vibrational levels $E_{\tau}$ exactly coincident with the desired energy $E$. The values of $\tau$ obeying this consistency requirement are the desired eigenchannel electronic eigenphases $\tau_{\alpha}$ [in fact these are the eigenphases denoted $\mu_{\alpha}$ in Eq. (2.4)]. The "unobservable" body-frame quantum defect $\mu(\epsilon, R)$ is transformed into "observable" laboratory-frame eigenchannel quantum defects $\tau_{\alpha}(E)$.

We will give in detail our reformulation of the above Greene-Jungen method in terms of logarithmic derivative $\zeta(\epsilon, R)$ defect, and will show how this reformulation will get around some of the difficulty in the above $\mu(\epsilon, R)$ formulation. A model study using this method[23] is described in the following to demonstrate some important aspects encountered in real electron-molecule scattering problems.

3.1 R-matrix formulation of the Greene-Jungen Method

The Greene-Jungen energy-dependent vibrational frame transformation method was originally formulated in terms of the reaction matrix or quantum defect function $\mu(\epsilon, R)$.[21] We have reformulated this method more directly in terms of the eigenchannel $R$-matrix approach of Fano and Lee.[11] The advantage of using the logarithmic derivative, or $R$ matrix, is that aside from the Born-Oppenheimer approximation, no other approximation is used to obtain the short-range $R$ matrix. In particular, the energy dependence of $(f, g)$ is neglected in the original treatment of Greene and Jungen to obtain the frame transformation matrix.[21,23] This approximation can be avoided
in the present reformulation. We also show below that in the $R$-matrix formulation, the normalization of the electronic wave function becomes simpler.

The spirit of the $R$-matrix method\cite{49,11,22} is that the short-range correlations, while complicated, are confined in a small finite region of space and can therefore be described by a complete discrete set of eigenstates even though the scattering state is a continuum state. At the reaction zone surface, these short-range eigenstates, called the $R$-matrix eigenstates, have $R$-independent electronic logarithmic derivatives which serve as the initial conditions for the solutions in the outer region. The method is thus easy to combine with a MQDT treatment in the long range.

A short-range $R$-matrix eigenstate is assumed to be a single Born-Oppenheimer product, as before. The clamped-nuclei $(N + 1)$ electronic wave function $\phi^{(e)}(N + 1)$ is first solved within the reaction zone. Instead of the ordinary quantum defect $\mu(\epsilon, R)$, we define the $\zeta(\epsilon, R)$ defect in terms of the negative logarithmic derivative of the outer electron wave function $\varphi(r; R)$ at $r_0$:

$$
\tan \pi \zeta(\epsilon, R) = -\frac{1}{\varphi(r; R)} \frac{\partial \varphi(r; R)}{\partial r} \bigg|_{r=r_0}.
$$

(3.4)

Here again we ignore electronic excitations so that

$$
\phi^{(e)}(N + 1) = A^\frac{1}{r} \phi^{(e)}(N) \varphi(r; R),
$$

(3.5)

where $\phi^{(e)}(N)$ is the target electronic wavefunction including also the angular wavefunction of the outer electron. The $\zeta(\epsilon, R)$ plays the same role as $\mu(\epsilon, R)$ does in the $K$-matrix representation, and contains all the short range information about the system required in this $R$-matrix formulation. They
are related by the following equation:

\[
\tan \pi \zeta(\epsilon, R) = -\frac{f^{0'}(r_0) - g^{0'}(r_0) \tan \pi \mu(\epsilon, R)}{f^{0}(r_0) - g^{0}(r_0) \tan \pi \mu(\epsilon, R)},
\]  

\( (3.6) \)

where \((f^0, g^0)\) are regular and irregular basis functions (analytic in energy) in the zero long-range field (see Sec. 2.1), and primes denote derivatives with respect to \(r\). We seek the electronic state with the following prescribed boundary condition:

\[
\zeta(\epsilon, R) = \tau.
\]

\( (3.7) \)

Similar to the \(K\)-matrix formulation, \(\tan \pi \tau\) is at this point an arbitrary \(R\)-independent parameter, but it will be identified as an \(R\)-matrix eigenvalue later. The body-frame electronic energy \(\epsilon(\tau)(R)\) for any given value of \(\tau\), can be extracted from the above equation.

Parallel to the \(K\)-matrix formulation, we can define the \(R\)-matrix eigenchannel potential curve \(V^{(\tau)}(R)\). Nuclei are allowed to move along this potential when the electron is close to the target. Vibrational energy levels and corresponding wave functions are solved which parametrically depend on the arbitrary phase \(\tau\). Requiring a vibrational energy level \(E^{(\tau)}_\alpha\) calculated in this potential curve to equal the total scattering energy \(E\) singles out a set of electronic eigenphases \(\tau_\alpha(E)\), the \(R\)-matrix "eigenphases".

In order to match the inner region solutions to the outer region close coupling solution, it is convenient at this point to introduce the "rotated" base pair\[14\]

\[
f^0(r) = \sqrt{\frac{\pi}{2}} \cdot f^0(r) g^0(r) - g^0(r) f^0(r_0)],
\]

\( (3.8) \)

\[
g^0(r) = -\sqrt{\frac{\pi}{2}} \cdot f^0(r) g^0(r) - g^0(r) f^0(r_0)],
\]

\( (3.9) \)
On the one hand we have in terms of \((f^0, \tilde{g}^0)\) the following electronic wavefunction in the inner region:

\[
\varphi(r_0; R) = N_\alpha(R) [f^0_r(r_0) \cos \pi \zeta(\epsilon, R) - \tilde{g}^0_r(r_0) \sin \pi \zeta(\epsilon, R)],
\]

with \(N_\alpha(R)\) the normalization factor\(^{[50]}\) determined by

\[
\int_0^{r_0} |\varphi(r_0; R)|^2 dr = 1.
\]

On the other hand we can write similar to Eq. (2.4) the outer region wavefunction in the \(R\)-matrix representation, in the form

\[
\Psi_\alpha = N_\alpha A r^{-1} \sum_v \varphi_v C_{v\alpha} \left[ f^0_v(r) \cos \pi \tau_\alpha - \tilde{g}^0_v(r) \sin \pi \tau_\alpha \right] \quad r > r_0,
\]

where \(C_{v\alpha}\) is the \(R\)-matrix eigenvector. Matching the inner region and outer region wavefunction at \(r = r_0\) (note that \(f^0(r_0) = \sqrt{2/\pi}, \tilde{g}^0(r_0) = 0, f^0'(r_0) = 0, \tilde{g}^0'(r_0) = \sqrt{2/\pi}\)) gives

\[
N_\alpha(R) = (\partial \zeta(\epsilon, R)/\partial \epsilon)^{-1/2} |_{\epsilon = \epsilon(\tau_\alpha)(R)},
\]

\[
C_{v\alpha} = \frac{1}{N_\alpha} \int \chi_v(R) F(r_0)(R) N_\alpha(R) dR,
\]

\[
N_\alpha = \left( \int |F(r_0)(R) N_\alpha(R)|^2 dR \right)^{1/2}
\]

Like \(\mu(\epsilon, R), \zeta(\epsilon, R)\) here provides sufficient information for obtaining the \(R\)-matrix eigenvalues \(\tan \pi \tau_\alpha\) and orthonormal eigenvectors \(C_{v\alpha}\).

The inverse of the usual \(R\)-matrix, which is defined as

\[
(R^{-1})_{v'v} = \sum_\alpha C_{v\alpha} \tan \pi \tau_\alpha C_{v'\alpha},
\]

contains the information about the complicated short range interactions in the form of the logarithmic derivatives at \(r = r_0\). It can be used to specify
uniquely the outer region solutions. \( C_{\text{oa}} \) becomes a simple Franck-Condon integral when the \( R \)-dependence of the electronic wavefunction can be neglected. Finally, the \( K \) matrix is related to the \( R \) matrix through the relation

\[
K = (Rg' + g)^{-1}(Rf' + f),
\]

where for instance \( f \) is a diagonal matrix whose \( v \)-th element is \( f^0(\epsilon_0) \).

It is worth noting that the above \( R \)-matrix formulation is exact, except that the Born-Oppenheimer approximation is assumed within the reaction region. Specifically, the energy dependences of \((f, g)\) are included in the formulation. Besides, in the \( K \)-matrix formulation, the normalization factor of the electronic wavefunction

\[
\mathcal{N}(R) = \left( \frac{\partial \mu(\epsilon, R)}{\partial \epsilon} + \frac{1}{2} W \right)^{-1/2} \bigg|_{\epsilon = \epsilon(\epsilon_0)},
\]

with

\[
W = \left\{ \left( [f_\epsilon, \partial g_\epsilon / \partial \epsilon] + [g_\epsilon, \partial f_\epsilon / \partial \epsilon] \right) \times \sin \pi \mu(\epsilon, R) \cos \pi \mu(\epsilon, R) \right. \\
- [f_\epsilon, \partial f_\epsilon / \partial \epsilon] \times \cos^2 \pi \mu(\epsilon, R) \\
- [g_\epsilon, \partial g_\epsilon / \partial \epsilon] \times \sin^2 \pi \mu(\epsilon, R) \bigg\} \bigg|_{\epsilon = \epsilon_\text{o}}
\]

appears much more complicated than the one occurring in the \( R \)-matrix formulation, Eq. (3.13).[23]

### 3.2 A Model Study Using The Greene-Jungen Method

The energy-dependent vibrational frame transformation has been applied previously to resonant \( e-N_2 \) collisions.[21] In that special case, the phase shift could be transformed into a smoother function of \( R \) and \( \epsilon \) by eliminating the trivial energy dependence resulting from the long range wavefunctions \((f_\epsilon, g_\epsilon)\) at small radii (See Fig. 1 of Ref. [21]) In the following, we
describe calculations designed to treat an energy dependence resulting purely from short range interactions. (This part of the work can be found in Ref. [23].) The models are chosen so that they are simple enough for analytical work (Schrödinger equations for these models are exactly solvable) while still showing realistic phenomena observed in electron-molecule collisions.

We consider an s-wave electron scattered from a target molecule whose ground state potential energy curve is that of a harmonic oscillator. The Hamiltonian of the system can then be written as follows:

\[ H = h + T + V(r, R), \]  

where \( h = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{1}{2} \mu \omega^2 R^2 \) is the target Hamiltonian, with reduced nuclear mass \( \mu \) and frequency \( \omega \), (understood to act on the rescaled nuclear wavefunction \( \chi_u(R) \), and not on \( \chi_u(R)/R \)). \( R \) is the internuclear distance measured relative to the target equilibrium separation. \( T = -\frac{1}{2} \frac{\partial}{\partial \tau} r^2 \frac{\partial}{\partial \tau} \) is the kinetic energy of the s-wave projectile electron, and \( V(r, R) \) is the interaction between the electron and the target. Typical values for the nuclear mass \( \mu = 1000 \) a.u. and frequency \( \omega = 2\pi \times 0.002 \) are used in our calculations. As a crude model for electron-neutral scatterings, \( V(r, R) \) is assumed to have the following form:

\[ V(r, R) = \begin{cases} 
0, & r \geq r_0, \\
V_0(r, R), & r < r_0.
\end{cases} \]  

(3.21)

When the electron is outside the target \( (r > r_0) \), motions of the electron and of the target are independent — the system consists of a free electron and a harmonically oscillating target. Once the electron is inside the target \( (r < r_0) \), an electron-molecule complex is temporarily formed. The potential energy \( V(r, R) \) depends jointly on \( r \) and \( R \), implying a correlation between electronic
motion and nuclear motion. It is this coupling that permits energy to be transferred from the incident electron to the target. The electron is ultimately ejected to infinity, leaving the target in one of its excited vibrational states.

Two different cases have been studied by making extreme approximations for the short range interaction $V_0(r, R)$. These models are so simple that the exact solution can be obtained by directly solving the Schrödinger equation. Results of calculations using various methods can thus be compared with the exact solution.

### 3.2.1 Nonresonant case

The interaction is described by a square well with $R$-dependent well depth

$$V_0(r, R) = u(R)$$

as shown in Fig. 9(a). For further simplicity, we take $u(R)$ to be a linear function of $R$

$$u(R) = c_0 + c_1 R$$

Basically this model exemplifies one of the simplest attractive short range interactions.

When the electron is inside the reaction zone, the short range clamped-nuclei electronic wavefunction, for a given arbitrary body-frame energy $\epsilon$, is solved from

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial r^2} + u(R)\right] \psi(r; R) = \epsilon \psi(r; R) \quad r < r_0.$$  \hspace{1cm} (3.24)

The negative of the logarithmic derivative at $r = r_0$

$$\tan \pi \zeta(\epsilon, R) = \begin{cases} q \cot q r_0, & q^2 > 0, \\ |q| \coth |q| r_0, & q^2 < 0, \end{cases}$$

\hspace{1cm} (3.25)
Figure 9. Potentials used to model the electron-molecule interaction. (a) A simple square well for nonresonant scattering. (b) A square well with a barrier for resonant scattering.
is required to equal a prescribed value \( \tan \pi \tau \). The electron kinetic energy inside the reaction zone is given by \( \frac{1}{2}q^2 = \epsilon - u(R) \). The value of \( q \) for which \( \tau \) and \( \zeta(\epsilon, R) \) intersect (modulo 1), denoted \( q^{(\tau)} \), determines the special solution satisfying the given boundary condition (See Fig. 10). Due to an exact separability of electronic and nuclear wavefunctions at \( r < r_0 \) in this extremely simple model, \( q^{(\tau)} \) does not explicitly depend on the internuclear distance \( R \). (Note that this Hamiltonian is exactly separable for \( r < r_0 \) and also for \( r > r_0 \), but it is not separable for all \( r \), thus permitting vibrational excitation to occur.)

The body-frame electronic energy is extracted as a function of \( R \)

\[
e^{(\tau)}(R) = c_0 + \frac{1}{2}(q^{(\tau)})^2 + c_1 R.
\] (3.26)

The linearity of \( e^{(\tau)}(R) \) reduces the potential curve of the electron-molecule compound

\[
V^{(\tau)}(R) = \frac{1}{2}\mu \omega^2 R^2 + e^{(\tau)}(R)
\] (3.27)
to that of a shifted harmonic oscillator, with the minimum shifted in \( R \) by the same amount for different values of \( \tau \) in this case.

Vibrational energies and corresponding wavefunctions of the nuclei in the adiabatic potential curve \( V^{(\tau)}(R) \) are

\[
E^{(\tau)}(\alpha) = (\alpha + \frac{1}{2})\omega - \frac{c_1^2}{2\mu \omega} + c_0 + \frac{1}{2}(q^{(\tau)})^2,
\] (3.28)

\[
F^{(\tau)}(R) = \chi_\alpha(R + R_0), \quad \alpha = 0, 1, 2, \ldots,
\] (3.29)

with \( \chi_\alpha(R + R_0) \) the shifted harmonic oscillator wavefunction and \( R_0 = c_1/\mu \omega^2 \) the shift of the minimum. Each vibrational energy level \( E^{(\tau)}(\alpha) \) must equal the given total energy \( E \), i.e.,

\[
E^{(\tau)}(\alpha) = E.
\] (3.30)
Figure 10. The body-frame electronic phase parameter $\zeta(\epsilon, R)$ is plotted as a function of the body-frame energy for a simple square well. The constraint that $\zeta(\epsilon, R)$ equals $\tau$, a constant independent of $R$, identifies the phase-dependent body-frame energy $\epsilon^{(\tau)}(R)$. 
It can be seen from Eq. (3.28) that for a given $\alpha$ only one value of $r$, $r_\alpha(E)$, will meet the above requirement. The eigenchannel potential curve $V^{(r_\alpha)}(R)$ is singled out by the coincidence of its $\alpha$-th vibrational energy level with the total energy $E$. In Fig. 11, several eigenchannel potential curves are plotted for $E = 0.03a.u.$ For this simple model no iteration is necessary because the electronic eigenstates can be directly found from Eq. (3.30) combined with Eq. (3.28), i.e.,

$$q^{(r_\alpha)^2} = 2[E - (\alpha + \frac{1}{2})\omega + c_1^2/2\mu\omega^2 - c_0]. \tag{3.31}$$

The $q^{(r_\alpha)}$ calculated using this equation gives the electronic wavefunction which satisfies the desired boundary condition

$$\tan \pi r_\alpha = \begin{cases} q^{(r_\alpha)} \cot q^{(r_\alpha)}r_0, & q^{(r_\alpha)} > 0, \\ |q^{(r_\alpha)}| \coth |q^{(r_\alpha)}|r_0, & q^{(r_\alpha)} < 0. \end{cases} \tag{3.32}$$

The $R$-matrix eigenvectors $C_{\alpha\alpha}$, given by

$$C_{\alpha\alpha} = \int \chi_\alpha(R)F^{(r_\alpha)}(R)dR, \tag{3.33}$$

are overlap integrals projecting oscillator states onto shifted oscillator states with the same frequency. An analytical expression for $C_{\alpha\alpha}$ valid for $\alpha \geq \nu$ is given in terms of a confluent hypergeometric function by

$$C_{\alpha\alpha} = \frac{1}{(\alpha - \nu)!} \sqrt{\frac{2^\nu\alpha!}{2^\nu\nu!}} \left( \frac{c_1}{\sqrt{\mu\omega^3}} \right)^{\alpha - \nu} \exp(\frac{-c_1^2}{4\mu\omega^3}) F_1(-\nu, \alpha - \nu + 1, \frac{c_1^2}{2\mu\omega^3}), \tag{3.34}$$

$$C_{\alpha\nu} = (-1)^{\alpha - \nu} C_{\alpha\alpha}. \tag{3.35}$$

For more general results the reader may refer to Ref. [51].

The $R$ matrix contains all the information about the short range interactions in the form of the logarithmic derivatives of the different independent solutions at the reaction zone surface. Following the standard
Figure 11. Eigenchannel potential curves for a given total energy $E=0.03$ a.u. are shown vs the internuclear separation $R$, measured relative to the target potential curve minimum, as the solid curves. Each curve has one vibrational energy level equal to $E$. The target potential curve and its vibrational levels are also shown as dashed curves. These curves are plotted for $c_1 = 0.01$, $r_0 = 3$. 
MQDT procedures described in Chapter 2, the transition probability $|S_{10}|^2$
for $v = 0$ to $v = 1$ vibrational transitions of the target is calculated. The co-
efficient $c_0$ is chosen so that the well just supports one bound state at $R = 0$.
Because we are particularly interested in relatively strong energy-dependence
of $\zeta(\epsilon, R)$, we use a large $r_0(=8 \text{a.u.})$ and small $c_1(=0.01)$ (See Sec. 3.2.3).
Fig. 10 clearly shows the strong energy dependence but weak $R$ dependence
of $\zeta(\epsilon, R)$. The other limit of weak energy dependence will be discussed in
Sec. 3.2.3.

In order to study the importance of the energy-dependence, we
also carry out calculations using the energy-independent vibrational frame
transformation.[6,8] The $K$ matrix calculated according to Eq. (2.26) is in-
dependent of the energy of the incident electron. A third method we use
for comparison is an "energy-modified" approach, which includes the energy
dependence in an approximate way — the arithmetic mean of the channel
energies, i.e., $\bar{\epsilon} = (\epsilon_v + \epsilon_v')/2$ with $\epsilon_v = E - E_v$, is used in Eq. (2.26). This
is similar to the idea of Nesbet's energy modified adiabatic method,[26] al-
though Nesbet instead advocates use of the geometric mean $\epsilon = \sqrt{\epsilon_v \epsilon_v'}$. Use
of the arithmetic mean enables us to include closed channel ($\epsilon_v < 0$) effects,
while correctly describing the Wigner threshold behavior also. The resulting
$K$ matrix thus acquires a dependence on the energy.

Transition probabilities obtained using various methods are shown
in Fig. 12. Fig. 13 shows the errors of results using above methods rel-
ative to the exact solution. It clearly shows the improvement of results
when the energy-dependence is taken into account, although even the energy-
dependent treatment is accurate to within about 10% for this nonresonant
Figure 12. Transition probability from $v=0$ to $v=1$, for the nonresonant square well. The solid curve is calculated by the energy-dependent vibrational frame transformation method which is exact for this problem, the chain-dotted curve uses the energy-modified vibrational frame transformation method, and the dashed curve uses the energy-independent vibrational frame transformation.
Figure 13. Comparison of the error in the calculated transition probabilities for nonresonant model, using the energy-independent vibrational frame transformation method (EIVFT), the energy modified vibrational frame transformation method (EMVFT), and the energy-dependent vibrational frame transformation method (EDVFT). The differences between the result of these methods and the exact calculation are shown.
model. For this model the energy-dependent vibrational frame transformation can be shown to be exact, at least when the version of Sec. 3.1 is used in place of the original Greene-Jungen treatment.[21]

3.2.2 Resonant case The interaction in this case is described by a square well with a barrier, with both the well depth and barrier height dependent on $R$ as shown in Fig. 9(b)

$$V_0(r, R) = \begin{cases} 
  v(R), & 0 < r < r_1, \\
  w(R), & r_1 < r < r_0. 
\end{cases}$$

(3.36)

Here again $v(R)$ and $w(R)$ are assumed to be linear functions of $R$ with adjustable coefficients: $v(R) = a_0 + a_1 R; w(R) = b_0 + b_1 R$. This model simulates a shape resonance in an electron-molecule collision. Normally the barrier formed in the effective potential of an electron-molecule system is centrifugal in nature.[52,53] When scattering at a resonant energy, the electron builds up a large probability density inside the target. The long time spent by the electron inside the molecule is associated with a strong energy dependence of the phase shift.

The inner region electronic wavefunctions are solved and the logarithmic derivative at $r = r_0$ is given by

$$- \tan \pi \zeta(\epsilon, R) = q \frac{pr_1 \cot ([r_0 - r_1]q) \cot pr_1 - qr_1}{qr_1 \cot ([r_0 - r_1]q) + pr_1 \cot pr_1},$$

(3.37)

where $p^2 = 2(\epsilon - v(R)), q^2 = 2(\epsilon - w(R))$. A sudden rise of $\zeta(\epsilon, R)$ by unity associated with the shape resonance is shown in Fig. 14. Imposing the eigenchannel condition $\zeta(\epsilon, R) = \tau$ selects the relevant electronic eigenstate potential curves $\epsilon^{(r)}(R)$. An iteration method is applied to select eigenchannel phase shifts $\tau_\alpha$ by requiring each vibrational energy level $E^{(r)}_\alpha$ to coincide
Figure 14. Body-frame electronic phase parameter $\zeta(\epsilon, R)$ is plotted as a function of the body-frame energy $\epsilon$ for a square well with a barrier, showing a sharp resonance feature.
with the desired scattering energy $E$. We construct the eigenvectors $C_{\nu\alpha}$ and then the $R$ matrix according to Eq. (3.14) and (3.16). This is followed by a multichannel quantum defect calculation of the vibrational excitation probabilities.

Exact solution for this resonant model can be obtained to be compared with the energy-dependent calculation. The scattering probability shown in Fig. 15 was calculated using the following parameters: $a_1 = 0, a_0 = -0.32; b_1 = 0.02, b_0 = 0.6; r_1 = 3, r_0 = 5$. The difference between the exact calculation and the energy-dependent frame transformation is shown in Fig. 16, which gives a relative error less than 2% throughout the range shown. A possible reason for this residual discrepancy will be given in Sec. 3.2.3.

3.2.3 Discussion We have shown that the energy-dependent vibrational frame transformation method can be successfully applied to treat a class of electron-molecule scattering processes where the energy dependence of the body-frame scattering parameters is substantial. But when the energy dependence becomes weaker and weaker, we must ascertain how this method merges with more conventional methods. We have studied this limit using the nonresonant model.

With the nonresonant model, two limiting cases can be realized by choosing model parameters like $r_0, c_1, c_0$. The limit of strong energy dependence ($\partial \zeta / \partial \epsilon \gg \partial \zeta / \partial R$) has been described in the previous section, and the limit of strong $R$ dependence ($\partial \zeta / \partial R > > \partial \zeta / \partial \epsilon$) is the one we are going to consider next. For this simple model, the following equation

$$\frac{\partial \zeta}{\partial R} = -c_1 \frac{\partial \zeta}{\partial \epsilon}$$

(3.38)
Figure 15. The transition probability from \( v=0 \) to \( v=1 \) for the square well with a barrier.
Figure 16. The difference between the energy-dependent vibrational frame transformation treatment and the exact calculation for the resonant model.
can be derived relating the $R$ dependence of $\zeta(\epsilon, R)$ to the $\epsilon$ dependence. The limit of weak energy dependence can be achieved by reducing the size of the reaction zone ($r_0$) and increasing the well depth ($|c_0|$). [In our calculations, we always require one state to be barely bound in the well when $R=0$. This automatically gives a restriction on $r_0$ and $c_0$, i.e., $-2c_0r_0^2 = (\pi/2)^2$.] This will decrease the collision time of the electron with the target. From Eq. (3.38), we can see that a large value of $c_1$ must be chosen to obtain an appreciable $R$ dependence when $\partial\zeta/\partial\epsilon$ is very small. The opposite case — the limit of strong energy dependence — can be accordingly obtained by taking large $r_0$ and small $c_1$, as we have described in Sec. 3.2.1.

In the limit of weak energy dependence, $c_1$ becomes large. This leads to large shifts in the eigenchannel potential curves relative to that of the target ($R_0 = c_1/\mu\omega^2$). Only very high vibrational states of the eigenchannel potentials will contribute to the overlap integrals connecting to low vibrational excitation channels. For high vibrational states of a harmonic oscillator, the wavefunctions are rapidly oscillating in the classically allowed region (See Fig. 17). The most appreciable contribution to the overlap integral $C_{\nu\alpha}$ for low $\nu$ comes from the amplitude around the turning point of the eigenchannel potential curves, i.e.,

$$C_{\nu\alpha} = \int \chi_{\nu}(R)F^{(r_0)}(R)dR \sim \chi_{\nu}(R_\alpha),$$

where $R_\alpha$ is the internuclear distance at the relevant turning point in the potential curve $V^{(r_0)}(R)$. So as far as the overlap integral is concerned, the eigenchannel vibrational wavefunction $F^{(r_0)}(R)$ behaves roughly like the Dirac delta function $\delta(R - R_\alpha)$. For the $\nu = 0$ case, we have explicitly shown the relation between $C_{0\alpha}$ and $\chi_0(R_\alpha)$. In particular, $\chi_0(R_\alpha)$ and $C_{0\alpha}$ both
Figure 17. An eigenchannel potential curve and the corresponding eigenchannel vibrational wavefunction (solid curves) with large $a$ in the large $c_i$ limit for a given total energy $E$. The target potential curve (chain-dotted) and its first vibrational wavefunction (chain-dashed) are also plotted.
peak at a special value of $\alpha$ such that $R_0 - R_\alpha = 0$ and exponentially decrease for other $\alpha$'s. Expanding $\chi_0(R_\alpha)$ and $C_{0\alpha}$ about their maxima, we have up to the second order the following relation:

$$\frac{\chi_0(R_\alpha)}{C_{0\alpha}} \sim \sqrt{\frac{c_1}{\omega}}, \quad (3.40)$$

which verifies the approximation $F^{(\tau_\alpha)}(R) \sim \sqrt{\frac{\mu}{c_1}} \delta(R - R_\alpha)$. A similar relation is expected to be hold for high $v$ as well. At the same time $\tau_\alpha \rightarrow \zeta(R_\alpha)$ in this limit because the relevant $R$ value for which $\Psi_\alpha$ has appreciable amplitude is near $R = R_\alpha$. Accordingly the conventional vibrational frame transformation

$$(R^{-1})_{\nu\nu'} = \int \chi_\nu(R) \tan \pi \zeta(R) \chi_{\nu'}(R) dR \quad (3.41)$$

is recovered from Eq. (3.16).

In the limit of weak energy dependence, the incident electron moves through the target so fast that it does not change the target electron distribution much and directly transfers its energy to nuclear motion (direct vibrational excitation). As the energy dependence becomes stronger and stronger, the electron spends more and more time in the target so that the electrons can be redistributed to form an electron-target molecular compound. The dynamics of the compound system can be accurately described within the Born-Oppenheimer approximation using the eigenchannel potentials $V^{(\tau_\alpha)}(R)$. After vibrating for some time along these potentials, this complex is deexcited and the electron leaves the target vibrationally excited (resonant vibrational excitation).

The essential approximation made in the energy-dependent vibrational frame transformation is the assumption of a Born-Oppenheimer separation at short range. The validity of this approximation should always
be carefully investigated. In this treatment the orthogonality of the $R$-matrix eigenchannel wavefunctions is a direct test for the validity of the Born-Oppenheimer approximation because exact eigenchannel wavefunctions are always orthogonal over the reaction zone surface. If the Born-Oppenheimer approximation is exact, we can show that the resulting eigenchannel $R$-matrix wavefunctions are orthogonal, i.e., the following integral

$$\int |\Psi_{\alpha'} H \Psi_{\alpha} - \Psi_{\alpha} H \Psi_{\alpha'}| dr dR = 0$$

implies that the orthogonality integral then vanishes identically:

$$\int \Psi_{\alpha} \Psi_{\alpha'} \delta(r - r_0) dr dR = 0 \quad \alpha \neq \alpha'.$$

In the nonresonant model studied in this paper, the exact separability of the electronic and nuclear wavefunction within $r < r_0$ implies that the eigenchannel wavefunctions are exactly orthogonal. Actually even the eigenchannel vibrational wavefunctions are orthogonal. It can be easily shown from Eq. (3.3) that

$$\int F^{(\tau_\alpha)}(R) F^{(\tau_{\alpha'})}(R) [V^{(\tau_\alpha)}(R) - V^{(\tau_{\alpha'})}(R)] dr dR = 0 \quad \alpha \neq \alpha',$$

where $V^{(\tau_\alpha)}(R)$ is the $\alpha$th eigenchannel potential curve. For the nonresonant model, the eigenchannel potential curves have the same frequencies and the same shifts so that $V^{(\tau_\alpha)}(R) - V^{(\tau_{\alpha'})}(R)$ is a constant. This immediately gives the orthogonality of $F^{(\tau_\alpha)}(R)$. This result is clearly related to the $R$ independence of the electronic wavefunctions of the problem. But in general different eigenchannel potential curves are not parallel and have a different vibrational spectrum, as for the resonant model. The eigenchannel vibrational states are then no longer orthogonal because $V^{(\tau_\alpha)}(R) - V^{(\tau_{\alpha'})}(R)$ is a function of $R$. 
However, the total eigenchannel wavefunctions (i.e., including the electronic solution on the surface of the reaction zone) are always orthogonal as long as the Born-Oppenheimer separation can be made. In these cases this treatment should be quite accurate. The $R$ dependence of electronic eigenstates is significant for the resonant model problem because we take an unusually strong short-range resonance (See Fig. 14). The $R$-matrix eigenchannels are then only approximately orthogonal. (In the examples of Figs. 14 - 16, the orthogonality integrals are typically of order $10^{-4}$). When the $R$ dependence of the electronic wavefunction is substantial, adiabatic corrections and even nonadiabatic effects may become essential.

This treatment can be easily extended to include adiabatic corrections. With the normalization in Eq. (3.11), the eigenchannel potential including the adiabatic correction term can then be written as follows (for the model problems treated here),

$$V^{(r_0)}(R) = V_T(R) + \epsilon^{(r_0)}(R) + \frac{1}{2\mu} \int_0^{r_0} |\partial \phi^{(r_0)}/\partial R|^2 \, dr.$$  \hspace{1cm} (3.45)

The last term in the above equation is the adiabatic correction which can be easily evaluated. We have shown that the $R$-matrix eigenchannel wavefunctions are orthogonal, but only to within the accuracy of the adiabatic approximation. Any nonorthogonality can be attributed to nonadiabatic effects within $r < r_0$, which is the main limitation of the method.

Another disadvantage of this method is the iteration procedure needed for its implementation in the most general form. Except for some extremely simple dependences of $\mu(\epsilon, R)$ or $\zeta(\epsilon, R)$ on $\epsilon$ and on $R$, in which they can be parameterized by simple analytical forms as in Ref. [21], the iterative procedure for selecting the eigenchannel phaseshifts at each energy.
$E$ could be time consuming in some applications. Possibly this procedure can eventually be "streamlined" along the lines of Ref. [55] to give the energy dependence of the $R$ matrix more efficiently.

An important point asserted in Greene-Jungen method is that within the Born-Oppenheimer approximation, the short range body-frame quantum defect $\mu(\epsilon, R)$ provides sufficient information to calculate the full scattering matrix. It is shown in Sec. 3.2 [Eqs. (3.13) and (3.18)] that the value of the electronic wavefunction on the boundary $r = r_0$ is directly determined by $\mu(\epsilon, R)$ or $\zeta(\epsilon, R)$, verifying that no more information than $\mu(\epsilon, R)$ or $\zeta(\epsilon, R)$ is needed to obtain the $K$ matrix or $R$ matrix. Because the Born-Oppenheimer separation serves as a good approximation at short range for most electron-molecule collisions, the energy-dependent vibrational frame transformation provides an effective way to treat the energy-dependence of scattering parameters. When non-Born-Oppenheimer effects are important, knowledge of $\mu(\epsilon, R)$ or $\zeta(\epsilon, R)$ is not sufficient to determine the scattering matrix, because the eigenchannel electronic wavefunctions are needed inside $r < r_0$ in order to evaluate the adiabatic and nonadiabatic corrections (See the adiabatic correction term in Eq. (3.45) for example).
CHAPTER 4

ALTERNATIVE FORMULATION OF THE ROVIBRATIONAL FRAME TRANSFORMATION

As we discussed in the previous chapter, most theoretical treatments of electron-molecule resonant scattering introduce some kind of electron-molecule compound potentials to incorporate the strong coupling between the electrons and the nuclei. The energy-dependent vibrational frame transformation of Greene and Jungen,[21,23] described in the previous chapter, defines a set of eigenchannel compound potentials which are extracted from the body-frame quantum defect function $\mu(\epsilon, R)$. In this chapter, we present, also within the framework of multichannel quantum defect theory, an alternative energy-dependent rovibrational frame transformation approach.[36] We show that the definition of compound potentials is unnecessary, and that $\mu(\epsilon, R)$, along with the target Born-Oppenheimer potential curve, is all one needs to describe the coupling of electronic and nuclear motions during scattering. Thus this new treatment avoids complicated procedures (like iteration and inversion in the previous method) to give a simpler description. In what follows we first give the full formulation of this approach. Applications of this method to study rovibrational Rydberg levels of $\text{H}_2$, and the vibrational excitation of $\text{H}_2$ and $\text{N}_2$ by electron collision, are discussed at the end.
4.1 Formulation

We consider again a problem having a single electronic channel. The description of electronic excitation of the target within our approach is not yet understood, although the electronically elastic effects of higher-lying target states are fully included. Electronically inelastic channels have been treated by Raseev and co-workers[56], and by Ross and Jungen[57] in the content of MQDT, although both studies neglect the energy dependence of short-range scattering parameters. Following the usual MQDT treatment, we apply the Born-Oppenheimer approximation at small electron distances, and use a laboratory-frame close coupling expansion in the asymptotic region.

4.1.1 Inner Region Solutions

Our goal is to solve the Schrödinger equation inside the reaction zone at a given total energy $E$. The solution in this region is a Born-Oppenheimer product of an electronic wavefunction $\psi^{(e)}(N+1)$ and a nuclear wavefunction $F(\vec{R})$

$$\Psi = \psi^{(e)}(N+1)F(\vec{R}). \quad (4.1)$$

The electronic eigenstates are obtained first in the body-frame fixed on the nuclei (all electronic coordinates are referred to the body-frame)[58,8]

$$H^{(e)}\psi^{(e)}_A(N+1) = V^{(N+1)}_A(\vec{R})\psi^{(e)}_A(N+1), \quad (4.2)$$

with a definite electronic angular momentum component $\Lambda$ along the internuclear axis. Then the nuclear Schrödinger equation can be solved[58]

$$\left[ -\frac{1}{2\mu_N} \nabla^2_R + V^{(N+1)}_A(\vec{R}) + \frac{\Lambda^2 \cot^2 \theta}{2\mu_N R^2} + \frac{1}{\mu_N R^2 \sin \theta} \frac{\partial}{\partial \phi} \Lambda \frac{\partial}{\partial \phi} - E \right] F(R, \theta, \phi) = 0. \quad (4.3)$$
Here $H^{(e)}$ is the electronic Hamiltonian including the electronic kinetic energy, the interaction between each electron and the nuclei, the interaction between the electrons, and also the internuclear interaction. $R$ is the internuclear distance, $(\theta, \phi)$ are the angles determining the orientation of the internuclear axis with respect to the laboratory-frame, $\mu_N$ is the reduced nuclear mass. Writing $F(R, \theta, \phi) = \frac{1}{R} \chi(R) D^J_{\Lambda M}(\theta, \phi)$, the above equation reduces to the following two equations:

$$
\begin{align*}
\left[ \frac{1}{\sin \theta} \frac{c}{d\theta} \left( \sin \theta \frac{d}{d\theta} \right) + 2 \cot \theta M \Lambda - \frac{M^2}{\sin^2 \theta} + J(J + 1) - \Lambda^2 - \Lambda^2 \cot^2 \theta \right] \Theta^J_{\Lambda M}(\theta) &= 0 \\
\end{align*}
$$

and

$$
\begin{align*}
&\left[ -\frac{1}{2\mu_N} \frac{d^2}{dR^2} + V^{(N+1)}_{\Lambda}(R) + \frac{J(J + 1) - \Lambda^2}{2\mu_N R^2} - E \right] \chi(R) = 0,
\end{align*}
$$

where $J$ and $M$ are total angular momentum and its $z$-component of the whole system. $D^J_{\Lambda M}(\theta, \phi) = \frac{\exp(iM \phi)}{\sqrt{2\pi}} \Theta^J_{\Lambda M}(\theta)$ is the well known symmetric top function, describing the overall rotations of the entire molecular system in space.

Most approaches in the literature[27,10,29,30,21] treat resonances by solving the $(N+1)$-electronic wavefunction Eq. (4.2) with some prescribed boundary conditions at the reaction zone boundary $r = r_0$. The Greene-Jungen method,[21,23] for instance, requires the logarithmic derivative of the electronic wavefunction to equal an $R$-independent parameter $\tau$. In this manner electron-molecule compound potential curves $V^{(N+1)}_{\Lambda}(R)$ are defined. Our approach starts from a different point of view. For scattering problems, the boundary values of the electronic wavefunctions are usually not known in advance since the scattering electron is in a continuum state.
(although the wavefunction of the \( N \) target electrons is assumed to be negligible beyond \( r_0 \)). In other words, different compound potentials can be determined according to different given boundary conditions. This gives rise to a fundamental *arbitrariness* in specifying the fixed-nuclei energy of the \((N+1)\) electrons. [Of course not every \( V_{A}^{(N+1)}(R) \) will satisfy Eq. (4.5) for a given total energy \( E \), but there are still a continuously infinite number of choices.] Thus for a given total energy \( E \), there exist an infinite number of degenerate Born-Oppenheimer solutions to the full short-range Schrödinger equation, before boundary conditions are imposed on the scattering electron wavefunction. This enables us to single out any particularly convenient set of Born-Oppenheimer eigenstates from this infinitely degenerate set by choosing \( V_{A}^{(N+1)}(R) \) appropriately. It should be noticed that this degeneracy results purely from the arbitrariness which exists in specifying boundary conditions on the electronic wave functions. (This infinite degeneracy is related to the infinite number of \( R \) values, or of the conjugate vibrational channels, rather than to the partial-wave degeneracy familiar in electron-molecule scattering.)

As a matter of fact, the different compound potential-energy methods mentioned earlier each correspond to a different choice of \( V_{A}^{(N+1)}(R) \).

We identify a *particularly simple and convenient class* of short-range Born-Oppenheimer eigenstates at total scattering energy \( E \) from this infinite number of possible choices. The nuclear wavefunctions in this set are *required* to be those of target nuclei, i.e., we use a compound potential which is the potential curve of the molecular target \( V_{A0}^{(N)}(R) \) except for an \( R \)-independent constant \( \epsilon \):

\[
V_{A}^{(N+1)}(R) = V_{A0}^{(N)}(R) + \epsilon. \tag{4.6}
\]
Nuclear wavefunctions $\chi_{A\mathbf{J}v}(R)$ and their corresponding energy eigenvalues $E_{A\mathbf{J}v}$ can be obtained by solving Eq. (4.5) with the above target potential. Thus for each total energy $E$, $\epsilon$ is quantized according to

$$\epsilon_{A\mathbf{J}v} = E - E_{A\mathbf{J}v}.$$  

(4.7)

Since $\epsilon_{A\mathbf{J}v}$ is $R$-independent, our compound potential curves are parallel to that of the target.

This class of Born-Oppenheimer states consists of a very special representation of the short-range compound states: When the electron is in the vicinity of the molecular target, the nuclei continue to move along the target potential curve as if they did not experience any force due to the scattering electron. This description of the short-range physics is especially simple despite the fact that the interaction between the scattering electron and the target is complicated and strong in this region of space. Since the potential curve of the target is usually known, one needs no additional effort to evaluate the compound potential-energy curves nor their vibrational wave functions.

In the body-frame, when the scattering electron leaves the core ($r > r_0$), a Born-Oppenheimer electronic wavefunction can be written as

$$\psi^{(s)}_{A\mathbf{J}v}(N + 1) = A\psi^{(s)}_{A\mathbf{J}v}(N)\frac{e^{-1}}{r} \sum_l Y_{l\mathbf{A}}(\vartheta', \varphi') f_{l\mathbf{A}Jv}(r) c_{l\mathbf{A}}(\epsilon_{A\mathbf{J}v}, R) -$$

$$g_{l\mathbf{A}Jv}(r) s_{l\mathbf{A}}(\epsilon_{A\mathbf{J}v}, R),$$  

(4.8)

where $\psi^{(s)}_{A\mathbf{J}v}(N)$ is the target electronic state (for simplicity, we assume $\mathbf{A}_0 = 0$, i.e., a $\Sigma$ target electronic state), and $(f_{l\mathbf{A}Jv}, g_{l\mathbf{A}Jv})$ are regular and irregular radial solutions (evaluated at the asymptotic energy $\epsilon_{A\mathbf{J}v}$) of the outer electron in the appropriate long range field of the target, $Y_{l\mathbf{A}}(\vartheta', \varphi')$ is the
angular wavefunction of the outer electron (primes indicate that the angles are referred to the body-frame). The matrices $c^A$ and $s^A$ contain all the information about the interaction between the incident electron and the target in the body-frame, and can be obtained from \textit{ab initio} calculations.

Our special Born-Oppenheimer eigenstates for $r \geq r_0$ can be written as:

$$
\Psi^{JM}_{i',\Lambda^L} = A\phi^{(e)}_{\Lambda^L}(N) \sum_{i} X^{(iA)}_{JM}(\hat{r}', \hat{R}) \times 
$$

$$
\left[ f_{i\Lambda^L}(r) c^{A}_{ij}(e_{\Lambda^L}, R) - g_{i\Lambda^L}(r) s^{A}_{ij}(e_{\Lambda^L}, R) \right]. \quad (4.9)
$$

Here again $X^{(iA)}_{JM}(\hat{r}', \hat{R})$ is an eigenfunction of total angular momentum with the outer electron angular wavefunction in the body-frame, as in Eq. (2.24). It should be noted that although we are writing a Born-Oppenheimer eigenstate in the outer region, we will only use this solution in the vicinity of the reaction surface.

### 4.1.2 Energy-dependent frame transformation

In the outer region, the Born-Oppenheimer separation no longer serves as a good approximation. A full laboratory-frame description should be used. The independent solution in this region is expanded in terms of a complete set of eigenstates of the target together with the outer electron's angular wavefunction:

$$
\Psi^{JM}_{i'\Lambda^L} = A\phi^{(e)}_{\Lambda^L}(N) r^{-1} \sum_{iN^+v^+} \frac{X^{(i\Lambda^L)}_{JM}(\hat{r}, \hat{R})}{R} \times 
$$

$$
\left[ f_{iN^+v^+}(r) I_{iN^+v^+,\Lambda^L} - g_{iN^+v^+}(r) J_{iN^+v^+,\Lambda^L} \right]. \quad (4.10)
$$
where the $\chi_{N^+v^+}(R)$ are the target nuclear eigenfunctions. The $I$ and $J$ matrices, containing all the scattering information required in the laboratory-frame, are obtained by matching the above equation to the inner region solution, Eq. (4.9), at $r = r_0$. The rovibrational frame transformation matrices can be obtained as follows:

$$I_{IN^+v^+t'\Lambda v} = \frac{2}{\pi} U_{N^+\Lambda}^{(lJ)} \left[ f_{IN^+\Lambda v}, g_{IN^+v^+} \right] | C_{IN^+v^+t'\Lambda v} - [g_{t'\Lambda v}, g_{IN^+v^+}] S_{IN^+v^+t'\Lambda v} \right), \tag{4.11}$$

$$J_{IN^+v^+t'\Lambda v} = \frac{2}{\pi} U_{N^+\Lambda}^{(lJ)} \left[ f_{IN^+\Lambda v}, f_{IN^+v^+} \right] | C_{IN^+v^+t'\Lambda v} - [g_{t'\Lambda v}, f_{IN^+v^+}] S_{IN^+v^+t'\Lambda v} \right), \tag{4.12}$$

where $[f, g]$ denotes a radial Wronskian evaluated at $r_0$.

The above equations consist of two parts: rotational and vibrational parts. The rotational frame transformation ($U_{N^+\Lambda}^{(lJ)}$) is simply a trivial geometrical transformation since it relates an angular momentum eigenstate relevant in the inner region (where $\Lambda$ is a good quantum number) to one relevant in the outer region (where $N^+$ is a good quantum number). The vibrational frame transformation is accomplished by the following integrations of the short-range scattering parameters $c_{N^+\Lambda v}$ and $s_{N^+\Lambda v}$ over vibrational wavefunctions of the target:

$$C_{IN^+v^+t'\Lambda v} = \int \chi_{N^+v^+}(R) c_{N^+\Lambda v}^A(\epsilon_{\Lambda Jv}, R) \chi_{\Lambda Jv}(R) dR, \tag{4.13}$$

$$S_{IN^+v^+t'\Lambda v} = \int \chi_{N^+v^+}(R) s_{N^+\Lambda v}^A(\epsilon_{\Lambda Jv}, R) \chi_{\Lambda Jv}(R) dR. \tag{4.14}$$

It should be noted that both $\chi_{N^+v^+}(R)$ and $\chi_{\Lambda Jv}(R)$ are evaluated in the same target potential $V_{N^+}(R)$. But $\chi_{N^+v^+}(R)$ is calculated with $J$ replaced by $N^+$ and $\Lambda$ by $\Lambda_0$ in Eq. (4.5). Finally the short-range reaction matrix can
be formed as $K = JI^{-1}$, and the closed channels can be "eliminated" in the usual sense of MQDT.

If only one partial wave of the outer electron is dominant in the asymptotic region, then $c^\Lambda$ and $s^\Lambda$ reduce to

$$
e^\Lambda(\epsilon, R) = N^\Lambda(\epsilon, R) \cos \pi \zeta^\Lambda(\epsilon, R), \quad (4.15)$$
$$s^\Lambda(\epsilon, R) = N^\Lambda(\epsilon, R) \sin \pi \zeta^\Lambda(\epsilon, R), \quad (4.16)$$

where $\zeta^\Lambda(\epsilon, R)$ is the body-frame logarithmic derivative and the normalization factor $N^\Lambda(\epsilon, R)$ is determined from $N^\Lambda(\epsilon, R) = (\partial \zeta^\Lambda / \partial \epsilon)^{-1/2}|_{\epsilon = \epsilon_v}$. Or in some applications the quantum defect $\mu(\epsilon, R)$ can be used if evaluations of the corresponding normalization factor, as given in Eqs. (3.18) and (3.19), can be simplified. Moreover, for purely vibrational interactions, Eq. (4.11), for instance, reduces to

$$I_{v^+v^+'} = [f_{v^+'}, g_{v^+}] C_{v^+v^+'} - [g_{v^+'}, g_{v^+}] S_{v^+v^+'}, \quad (4.17)$$

where

$$C_{v^+v^+'} = \int \chi_{v^+'}(R) N(\epsilon_{v^+'}, R) \cos \pi \zeta(\epsilon_{v^+'}, R) \chi_{v^+}(R) dR. \quad (4.18)$$

A similar expression holds for $S_{v^+v^+'}$, except with cos replaced by sin.

4.1.3 Discussion  The special choice made for the inner region Born-Oppenheimer solutions enables us to obtain the rovibrational frame transformation equations (4.11)-(4.14), which include the energy dependence of the short-range scattering parameters in a very simple and explicit way. Furthermore, the energy dependence of $(f, g)$, if important, is also included in the frame transformation. When this energy dependence can be neglected,
as assumed in most of the initial frame transformation studies, we find
\[ I_{N^+u^+,v',\Lambda^v} \rightarrow \frac{2}{\pi} U_{N^+\Lambda}^{(IJ)} C_{IN^++v',J^+\Lambda^v}, \text{ and } J_{IN^++v',J^+\Lambda^v} \rightarrow \frac{2}{\pi} U_{N^+\Lambda}^{(IJ)} S_{IN^++v',J^+\Lambda^v}. \]
It can be shown that the energy-independent rovibrational frame transformation in Chapter 2 is a special case of the present approach. In the limit of weak energy dependence (and consider a single partial wave in the outer region), we have
\[
I_{N^+u^+,\Lambda^v} = U_{N^+\Lambda}^{(IJ)} \int \chi_{N^++v^+}(R)N_{\Lambda}(R) \cos \pi \mu_{\Lambda}(R)\chi_{\Lambda J^v}(R)dR. \quad (4.19)
\]
Multiplying the above equation by \[U_{N^+\Lambda}^{(IJ)} \int \chi_{N^++v^+}(R')\chi_{\Lambda J^v}(R')dR'\] and summing over \(v\) and \(\Lambda\) gives
\[
I_{N^+u^+,N'^+v'^+} = \sum_{\Lambda} I_{N^+u^+,\Lambda^v} < \chi_{\Lambda J^v} | \chi_{N'^+v'^+} > U_{N^+\Lambda}^{(IJ)}
= \sum_{\Lambda} U_{N^+\Lambda}^{(IJ)} < \chi_{N^++v^+} | N_{\Lambda}(R) \cos \pi \mu_{\Lambda}(R) | \chi_{N'^+v'^+} > U_{N^+\Lambda}^{(IJ)}.
\]
(4.20)
It should be noted that the completeness condition \(\sum_v |\chi_{\Lambda J^v} > < \chi_{\Lambda J^v}| = 1\) is needed to derive Eq. (4.20), but this cannot be used analogously in Eq. (4.13), because of the energy dependence of the quantum defect. The reaction matrix constructed according to \(JI^{-1}\) reduces to the familiar form as in the Eq. (2.26) in Chapter 2. The normalization factor \(N_{\Lambda}\) drops out in this limit if the vibrational basis is complete.

In the energy-dependent vibrational frame transformation method in the previous chapter, Greene and Jungen define a class of potential-energy curves of the electron-molecule complex, as given in Eq. (3.1). This potential is extracted from the body-frame quantum defect function \(\mu(\epsilon, R)\) by "inverting" the constraint \(\mu(\epsilon, R) = \tau\), with \(\tau\) an arbitrary \(R\)-independent
eigenphase parameter. An iteration procedure must then be used to select special values of the phase parameter $\tau_\alpha(E)$ for each given total energy $E$ such that the compound potential curve has its $\alpha$th vibrational energy level coincident with the given energy $E$. Except for a limited number of simple forms for the energy dependence of the quantum defect, this method becomes cumbersome to implement. The present method, however, bypasses the concept of the compound potential energy curves (more precisely, our compound potential is the target potential), which avoids the iteration, inversion, and other complications in the previous method to give a simpler and more transparent method to incorporate effects of the body-frame energy dependence. Since $\mu(\epsilon, R)$ contains all the information one needs, along with the target potential curve, it is unnecessary to extract any compound potential from $\mu(\epsilon, R)$. Another advantage of the present method is that the energy-independent frame transformation is naturally recovered in the weak energy-dependent limit from the more general energy-dependent case, as shown in Eqs. (4.20). This limit is less obvious formally (and even more difficult to demonstrate numerically) in the previous formulation, as can be seen from Sec. 3.2.3 of Chapter 3.

A drawback of our treatment is that the rovibrational frame transformation matrices $I$ and $J$ need to be evaluated for each given total scattering energy $E$ for the most general energy dependence of $\mu(\epsilon, R)$ or $\zeta(\epsilon, R)$. This could become time consuming in some applications. But in many cases, the energy dependence of $\mu(\epsilon, R)$ (or $\zeta(\epsilon, R)$) can be fitted to simple analytical forms, as demonstrated below in the vibrational excitation of $N_2$ by electron
impact (where a Breit-Wigner profile is used to describe the energy dependence) and in calculations of rovibrational energy levels of H$_2$ (where a linear energy dependence can be used). Thus the energy is factored out of the integrations, which consequently can be obtained once and for all. Another disadvantage of this treatment is that the direct extension of this method to include dissociation is not obvious. However, we will show in the next chapter that the current Born-Oppenheimer eigenstates, together with the frame transformation wavefunctions, can be used as basis functions in a variational $R$-matrix treatment of competing ionization and dissociation processes.

4.2 Vibrational excitation in of e-N$_2$ d$\pi_g$ resonant scattering

The first application of this rovibrational frame transformation method to be discussed involves the vibrational excitations of N$_2$ by electron impact. This system has been studied extensively both theoretically and experimentally.[27,59,7] It is well known that the d$\pi_g$ negative ion resonant state dominates the excitation processes. Greene and Jungen[21] calculated vibrational excitation cross sections for this system using their energy dependent vibrational frame transformation method. Thus this system provides us with an important test case for our method.

The Breit-Wigner profile is used to approximate the energy dependence of the scattering phase shift $\mu_0(\epsilon, R)$, as inRefs. [59,21]:

$$\tan \pi \mu_0(\epsilon, R) = \frac{-\Gamma_0(R)}{2|\epsilon - \epsilon_0(R)|}.$$  \hspace{1cm} (4.21)

Here $\mu_0(\epsilon, R)$ is the $l = 2$ phase shift referred to the analytical long-range base pair ($f^0, g^0$). The energy dependence of this base pair, which vanishes in the limit of $r \to 0$, is neglected since the reaction zone radius is small.
Due to the simple energy dependence of $\mu^0(\epsilon, R)$ and $N(\epsilon, R)$, the $I$ and $J$ matrices can be calculated in the following way:

\[
I_{v'\rightarrow v''} = \epsilon_{v''} \int \chi_{v''}(R) \left[ \frac{2\pi}{\Gamma^0(R)} \right]^{1/2} \chi_{v''}(R) dR \\
- \int \chi_{v''}(R) \left[ \frac{2\pi}{\Gamma^0(R)} \right]^{1/2} \epsilon_0(R) \chi_{v''}(R) dR, \tag{4.22}
\]

\[
J_{v'\rightarrow v''} = - \int \chi_{v''}(R) \left[ \frac{\pi \Gamma^0(R)}{2} \right]^{1/2} \chi_{v''}(R) dR. \tag{4.23}
\]

All integrals in these equations are independent of energy and need to be calculated only once. The reaction matrix is exactly symmetric in this case if a complete vibrational basis is included. It can be easily shown first that $K^{-1} (= L.J^{-1})$ is symmetric. We may write $I_{v'\rightarrow v''} = \epsilon_{v''} A_{v'\rightarrow v''} - B_{v'\rightarrow v''}$, where $A$ and $B$ are the first and second matrices in Eq. (4.22) and both are symmetric. $J^{-1}$ is exactly $-2A$. So we have

\[
(K^{-1})_{v'\rightarrow v''} = -2 \sum \epsilon_0 A_{v'\rightarrow v''}^* - B_{v'\rightarrow v''}^* (4.24)
\]

with

\[
(BA)_{v'\rightarrow v''} = (AB)_{v'\rightarrow v''} = \int \chi_{v'}(R) \frac{\epsilon_0(R)}{\Gamma^0(R)} \chi_{v''}(R) dR. \tag{4.25}
\]

Thus $K^{-1}$ (also $K$) is symmetric since both terms in Eq. (4.24) are symmetric.

Standard MQDT procedures are then used to calculate the probabilities $|S_{v0}|^2$ for vibrational excitations from the ground vibrational state $v = 0$ to excited vibrational states $v = 1$ to $v = 7$. The results are shown in Fig. 18. They agree with those obtained by Greene and Jungen\cite{21} to an accuracy of better than $10^{-6}$. The complicated modulations are signatures of the existence of the $d\pi_g$ compound state, which is a shape resonance. This
Figure 18. Cross sections for vibrational excitation of \( \text{N}_2 \) from \( v = 0 \) to \( v = 1, 2, \ldots, 7 \) using the present formulation (right) compared with the experimental (Ehrhardt and Willman, Ref. '60) and theoretically fitted (Ref. '59) cross sections (left), from Ref. '21'. The differences between present results and those of Greene and Jungen are not visible on the scale of this graph.
is a particularly striking verification of the validity of this approach, since all previous methods capable of quantitatively describing the e-N\textsubscript{2} resonant cross sections made use of some type of vibrational wave functions calculated in a compound potential curve, as in the boomerang model.\textsuperscript{[27]}

4.3 Rovibrational energy levels of low lying Rydberg states of H\textsubscript{2}

A second application has been made to a very different system: the rovibrational Rydberg bound levels of H\textsubscript{2}. This system provides another test of our frame transformation method, since it was originally formulated for scattering problems. As in all previous work, MQDT should permit a unified treatment of the continuum and bound Rydberg channels.

We calculated the rovibrational energy levels of H\textsubscript{2} in $B'$ ($2\Sigma_u^+$), $B''$ ($3\Sigma_u^+$), and $D$ ($3\Pi_u$) electronic states. Since a Rydberg electron in a $\Sigma$ state can penetrate deep into the core region, the energy dependence ($n$ dependence) of $\mu_\Sigma$ is stronger than that of $\mu_\Pi$. Accordingly we neglect the energy dependence of the $\Pi$ state, and fit the energy dependence of $\mu_\Sigma$ to a linear function of energy connecting the $B'$ and $B''$ states:

$$
\mu(\epsilon, R) = \mu_4\Sigma(R) + f(R)[\epsilon - \epsilon_4\Sigma(R)].
$$

(4.26)

Here $\epsilon_4\Sigma(R)$ and $\mu_4\Sigma(R)$ are the electronic energy and body-frame quantum defect of the $B''$ states, respectively. The slope $f(R)$ is thus given by $f(R) = [\mu_4\Sigma(R) - \mu_3\Sigma(R)]/[\epsilon_4\Sigma(R) - \epsilon_3\Sigma(R)]$. As in the calculation of N\textsubscript{2} vibrational excitations, we neglect the energy dependence of the long-range Coulomb functions $(f,g)$ ($l = 1$). Table 4.1 shows the first eight calculated $J = 0$ levels of the $B''$ state (levels with $v \geq 5$ are autoionizing states above the ionization threshold). For $J = 0$ states, there is no rotational coupling and
Table 4.1: Energy levels of $B''$ state of $H_2$, in cm$^{-1}$ ($J = 0$)

<table>
<thead>
<tr>
<th>$v$</th>
<th>Present</th>
<th>JA</th>
<th>Exptl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>116883.4</td>
<td>116885.2</td>
<td>116886.0</td>
</tr>
<tr>
<td>1</td>
<td>118945.1</td>
<td>118945.4</td>
<td>118945.0</td>
</tr>
<tr>
<td>2</td>
<td>120869.4</td>
<td>120869.9</td>
<td>120869.4</td>
</tr>
<tr>
<td>3</td>
<td>122659.3</td>
<td>122654.6</td>
<td>122656.4</td>
</tr>
<tr>
<td>4</td>
<td>124308.0</td>
<td>124307.7</td>
<td>124307.7</td>
</tr>
<tr>
<td>5</td>
<td>125853.3</td>
<td>125855.7</td>
<td>125850.2</td>
</tr>
<tr>
<td>6</td>
<td>127090.0</td>
<td>127096.7</td>
<td>127094.5</td>
</tr>
<tr>
<td>7</td>
<td>128307.6</td>
<td>128311.3</td>
<td>128306.8</td>
</tr>
</tbody>
</table>

Table 4.2: Energy levels of $B'$ state of $H_2$, in cm$^{-1}$ ($J = 1$)

<table>
<thead>
<tr>
<th>$v$</th>
<th>Present</th>
<th>JA</th>
<th>Exptl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>110528.8</td>
<td>110529.3</td>
<td>110528.93</td>
</tr>
<tr>
<td>1</td>
<td>112403.6</td>
<td>112404.7</td>
<td>112403.75</td>
</tr>
<tr>
<td>2</td>
<td>114117.2</td>
<td>114119.0</td>
<td>114118.25</td>
</tr>
<tr>
<td>3</td>
<td>115644.5</td>
<td>115647.7</td>
<td>115646.78</td>
</tr>
</tbody>
</table>

The levels are obtained by pure vibrational frame transformation using $\mu_\Sigma(R)$. 

In Tables 4.2 and 4.3, we show energy levels of the $B'$ and $D$ states for $J = 1$. In this case, we explicitly consider the coupling between $\Sigma$ and $\Pi$ states through the rovibrational frame transformation. For the most part, the energy-independent results of Jungen and Atabek (denoted JA in the tables)[8] are reproduced in all these calculations, showing how the small

Table 4.3: Energy levels of $D$ state of $H_2$, in cm$^{-1}$ ($J = 1$)

<table>
<thead>
<tr>
<th>$v$</th>
<th>Present</th>
<th>JA</th>
<th>Exptl.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>112934.7</td>
<td>112934.6</td>
<td>112935.5</td>
</tr>
<tr>
<td>1</td>
<td>115155.5</td>
<td>115155.3</td>
<td>115155.8</td>
</tr>
<tr>
<td>2</td>
<td>117251.3</td>
<td>117251.3</td>
<td>117251.6</td>
</tr>
<tr>
<td>3</td>
<td>119217.3</td>
<td>119218.6</td>
<td>119217.6</td>
</tr>
<tr>
<td>4</td>
<td>121064.0</td>
<td>121062.4</td>
<td>121062.4</td>
</tr>
<tr>
<td>5</td>
<td>122787.0</td>
<td>122787.4</td>
<td>122787.4</td>
</tr>
</tbody>
</table>
discrepancies between the experimental energy levels (denoted Exptl. in the tables)\cite{61} and the MQDT calculations of Jungen and Atabek are apparently not caused by their neglect of $\partial \mu / \partial \epsilon$.

### 4.4 Vibrational excitations of H$_2$ by electron collision

It has been known for some time that the H$_2^-$ ($^3\Sigma_u^+$) shape resonance at about 3eV incident electron energy plays a role in the vibrational excitation cross sections of H$_2$ by low energy electron scattering (below 5eV).\cite{7} Angular distribution measurements show that the scattering electron has mostly $p$-wave character. This resonance state is short-lived (having a decay width of several eV) at small internuclear distances $R$ and becomes a true bound state for $R > 3$ a.u. Therefore, there is no clear evidence of the existence of this resonant state in the elastic scattering cross section, as this probes the small-$R$ region where it is extremely broad. The study of rovibrational excitations and dissociative attachment helps to probe the large-$R$ region where the resonance is long-lived. Both theoretical studies based on resonance models,\cite{62,63} and on nonresonant descriptions,\cite{7} are present in the literature. Our study does not explicitly invoke a compound state, as we described earlier, although all the electronic and nuclear couplings are included in the quantum defect function in the form of its energy dependence, in addition to its $R$ dependence.

The calculation is based on an *ab initio* fixed-nuclei $l = 1$ quantum defect function $\mu(\epsilon, R)$, calculated very recently by Robicheaux.\cite{63} We follow a logarithmic derivative formulation using the $\zeta$-defect instead of $\mu(\epsilon, R)$, because $\zeta(\epsilon, R)$ is a monotonically-increasing function of energy. Moreover, by including the energy dependence of $(f, g)$ in $\zeta(\epsilon, R)$, we can avoid some
analytical complications in evaluating the normalization factor in the electronic wavefunction. Figure 19 shows the fixed-nuclei quantum defect \( \mu(\epsilon, R) \) and the corresponding logarithmic derivative \( \zeta(\epsilon, R) \) defect at \( r = 7 \) a.u. as functions of both the electronic energy \( \epsilon \) (measured from the \( \text{H}_2 \) ground electronic state) and the internuclear distance \( R \). It is seen that including the energy dependences of \((f, g)\) results in a much stronger energy dependence of \( \zeta(\epsilon, R) \).

Our reaction zone is chosen to be within the region \( r < 7 \) a.u. and \( R < 3.5 \) a.u. We do not explicitly consider rotational excitations in this treatment. The vibrational frame transformation can be carried out by evaluating the following matrix elements:

\[
C_{v'v''} = \int \chi_{v'}(R)N(\epsilon_{v'}, R)\cos \pi\zeta(\epsilon_{v'}, R)\chi_{v''}(R)dR \tag{4.27}
\]

with \( N(\epsilon_{v'}, R) \) given simply by \((\partial\zeta/\partial\epsilon)^{-1/2}|_{\epsilon=\epsilon_{v'}}\). A similar equation for \( S_{v'v''} \) can be obtained by replacing \( \cos \) by \( \sin \). With these energy-dependent frame transformation matrices, we may apply standard MQDT procedures to evaluate the final cross sections.

Fig. 20 gives our result for vibrational excitation from the ground vibrational level to the first and second excited levels. We show in Fig. 21 the vibrational excitation cross sections starting from excited initial states \( \text{H}_2(v) \). It is seen that the fine structures due to the negative ion state \( 2^2\Sigma_u^+ \) begin to emerge more clearly as \( v \) increases. Since the resonance state is so broad for small internuclear distances, the resonant structures can hardly be seen for lower excitations. However, for higher excitations, the nuclei can be stretched into the region where the resonance becomes long-lived. For higher excitations (\( v = 3 \rightarrow v = 4 \)), our results begin to differ from those of
Figure 19. Body-frame quantum defect $\mu(\epsilon, R)$ (a) and $\zeta(\epsilon, R)$ defect (at $r = 7\text{ a.u.}$) (b) are shown as functions of both body-frame electronic energy $\epsilon$ and internuclear distance $R$. 
Figure 20. Vibrational excitation cross section from $v = 0$ to $v = 1$ (a), and $v = 0$ to $v = 2$ (b). Present results (+) are shown along with the calculation of Robicheaux (—) using a modified Greene-Jungen method. Experimental results (○) are also shown. [64]
Figure 21. Vibrational excitation cross section in e-H₂ scattering, from \( v = 0 \) to \( v = 1 \) (solid lines), \( v = 1 \) to \( v = 2 \) (dashed lines), \( v = 2 \) to \( v = 3 \) (chain-dotted lines), and \( v = 3 \) to \( v = 4 \) (dotted lines). (a) Present calculation. (b) results calculated by Robicheaux.
Robicheaux. Part of the reason for this is that we neglect the dissociation process in our calculation. As vibrational states (either initial or final) become higher, dissociative attachment will increasingly play a significant role. The next chapter addresses the incorporation of such dissociative channels into this approach.
CHAPTER 5

PRELIMINARY STUDY OF IONIZATION AND DISSOCIATION PROCESSES

5.1 Introduction

The complexity of a molecular system derives largely from its multiple fragmentation channels.[7] In all preceding chapters, we described how to treat rovibrational couplings in the ionization (or electron detachment) channels in which one electron either remains in a high bound level, or else escapes to infinity in a continuum state. We discussed how the interchannel interaction affects the spectra and scattering processes, and how MQDT, with a frame transformation, is able to account for non-Born-Oppenheimer effects resulting from large electron distances or from a non-negligible time delay of the outer electron in the reaction zone. In this chapter, we are going to study how nonadiabatic effects cause the most basic reactive process — the conversion of electronic energy into nuclear motion, leading to dissociation of the molecule.

Molecular dissociation processes have been subjected to extensive theoretical and experimental studies.[65,17,31,62] Typical examples include the energy spectra of $\text{H}_2$ above the dissociation limit (predissociation)[66] and the competition between dissociation and ionization processes.[17] Fig. 22 shows potential energy curves of $\text{H}_2$ and $\text{H}_2^+$ which are relevant in this study. A particular level in the $D$ Born-Oppenheimer state, $(v = 3, J = 2)$
Figure 22. Potential curves of H$_2$ relevant to this study.
for example, lies above the H(1s) + H(2l) dissociation limit, and will predissociate through the interaction with the continua of the low lying $B'$, $C$, and $B$ electronic states. In the photoabsorption cross section, a clear Beutler-Fano profile, which is well known in atomic autoionization, will appear as a result of the interference between this indirect photodissociation through the bound level and the direct photodissociation channel. A Fano-profile analysis\cite{66} shows that the rotational (Coriolis) coupling of the $D$ and $B'$ states is responsible for the observed predissociation. Another typical example where dissociation plays an important role is the ionization process. Usually, ionization is a much more frequent process than dissociation since the electron is so much lighter and easier to excite than the nuclei. However, due to the coupling between electronic and nuclear degrees of freedom, a dissociative pathway can dominate in some cases (like dissociation-induced ionization).\cite{17,14}

In order to describe all of these complicated electronic and nuclear interactions occurring when ionizing and dissociating processes compete, Jun- gen proposed an eigenchannel $R$-matrix treatment.\cite{17} He showed that a body-frame quantum defect function $\mu_A(R)$ contains sufficient information to account for the coupling between electronic and nuclear degrees of freedom at short-range. As in all MQDT treatments, the configuration space is divided into several regions according to the different interactions dominant in these regions. In order to describe ionization and dissociation processes, we consider a two-dimensional configuration space spanned by the radial coordinate $r$ of the outer electron and the internuclear distance $R$ as in Fig. 23. The reaction zone (region I) is within the region $r < r_2$, $R < R_0$. Beyond $r_2$
(\(R_0\)), all relevant bound electronic (vibrational) wavefunctions are negligible. Specifically, \(r_2\) should be taken large enough to include not only the molecular core, but also the entire electronic states responsible for dissociation. Only the Rydberg electron is able to go beyond this region. Thus a laboratory-frame close coupling type expansion like in Eq. (2.1) or Eq. (2.4) can be used in region II. On the other hand, only the nuclear vibrational wavefunctions in the dissociation channels are allowed in region III where the nuclei separate along well-defined Born-Oppenheimer potential curves. Wavefunctions in region IV are required to vanish since the dissociative ionization process (\(h\nu + H_2 \rightarrow H + p + e\), for instance) is not fully understood within the MQDT description, and since they become important only at considerably higher energies than are treated here.

All the complicated electron-nuclei coupling is confined to this small region of space. In Jungen’s approach, the configuration space (region I)
along the electronic direction is further subdivided into three regions: $r_1$ is the distance at which the Born-Oppenheimer approximation starts to break down, while $r_0$ corresponds to the size of the ionic molecular core. A Born-Oppenheimer type eigenfunction is used within region $r < r_1, R < R_0$ while a laboratory-frame multichannel expansion is used in the region $r_1 < r < r_2, R < R_0$. A Fano-Lee type eigenchannel $R$-matrix calculation[11] is then set up in this region to determine the logarithmic derivatives ($R$-matrix eigenvalues) iteratively as we mentioned in previous chapters.

MQDT is then used to propagate the solution from region I to the asymptotic regions II and III in the relevant long-range fields using the given boundary conditions on the reaction zone surface. In this way, Jungen was able to account for the branching ratio of ionization to dissociation observed in the photoabsorption experiment of $H_2$.[18] Greene, using a related formulation,[14] was able to calculate the position and the predissociation linewidth of the $D (v = 3, J = 2)$ state, which are in good agreement with experimental results.[61]

A disadvantage of the Fano-Lee eigenchannel $R$ matrix approach, as we discussed in previous chapters, is the iteration procedure involved. We have reformulated an alternative treatment based on a noniterative $R$-matrix approach.[54] Since no iteration is needed in this new method, it should be more efficient to implement in numerical calculations. However, as this is only a preliminary study at this stage, future explorations will be required to fully understand the complicated interaction between electronic and nuclear motions. In what follows, we first summarize the noniterative eigenchannel $R$-matrix method.[54] The full theoretical formulation of our
method is presented, using the noniterative $R$-matrix method. Finally we show a few test calculations using this method.

5.2 Summary of the noniterative eigenchannel $R$-matrix method

We summarize in this section the noniterative eigenchannel $R$-matrix method [54] in the molecular context. The Hamiltonian for a molecular system can be written as

$$H = -\frac{1}{2\mu_N} \nabla_R^2 - \frac{1}{2m_e} \nabla_r^2 + V,$$

where the first term refers to the nuclear kinetic energy ($\mu_N$ is the reduced nuclear mass), the second term is the sum of kinetic energies of all electrons ($m_e$ is mass of the electron), and $V$ is potential energy between all particles in the system. We start from the well-known Ritz variational principle for energy eigenvalues of a many-particle system in the reaction zone volume $\Omega$:

$$E = \frac{\int_{\Omega} \Psi^* \left(-\frac{1}{2\mu_N} \nabla_R^2 - \frac{1}{2m_e} \nabla_r^2 + V\right) \Psi \, d\omega}{\int_{\Omega} \Psi \cdot \nabla \Psi \, d\omega}. \quad (5.2)$$

This equation can equally well be written as follows after applying Green's theorem:

$$E = \left[ \int_{\Omega} \left( \frac{1}{2\mu_N} \nabla_R \Psi^* \cdot \nabla_R \Psi + \frac{1}{2m_e} \nabla_r \Psi^* \cdot \nabla_r \Psi + \Psi^* V \Psi \right) \, d\omega \right. \left. - \frac{1}{2\mu_N} \int_{\Sigma_R} \Psi^* \frac{\partial \Psi}{\partial n} \, d\sigma_R - \frac{1}{2m_e} \int_{\Sigma_r} \Psi \frac{\partial \Psi}{\partial n} \, d\sigma_r \right] / \int_{\Omega} \Psi^* \Psi \, d\omega, \quad (5.3)$$

where the additional surface integrals are over the surface $\Sigma$ enclosing the reaction zone (with $\Sigma_r$ and $\Sigma_R$ denoting the $r = r_2$ and the $R = R_0$ surface, respectively), $\partial \Psi / \partial n$ is the normal derivative on the surface $\Sigma$. The eigenchannel $R$-matrix method of Fano and Lee [11,14] first determines a complete
set of discrete eigenstates for a given arbitrary (mass weighted) logarithmic derivative \( b \) on the reaction surface

\[
(\partial \Psi / \partial n + b \mu_n \Psi)_{\Sigma_R} = 0, \tag{5.4}
\]

\[
(\partial \Psi / \partial n + b m_e \Psi)_{\Sigma_e} = 0. \tag{5.5}
\]

For an arbitrary logarithmic derivative \( b \), the energies of these \( R \)-matrix eigenstates \( E_n(b) \) are generally not equal to the total scattering energy of the system \( E \). This method then selects, with the help of an iteration procedure, a set of \( b_\beta \) which yield eigenstates \( \Psi_\beta \) having the same desired total energy \( E \).

Rewriting Eq. (5.3) as

\[
\rho_n = -\frac{1}{\mu} \nabla_R \Psi^* \cdot \nabla_R \Psi - \frac{1}{m_e} \nabla_r \Psi^* \cdot \nabla_r \Psi - 2 \Psi^*(E - V)\Psi \]<

we find the above procedure is equivalent to varying the logarithmic derivative \( b \) at a constant scattering energy \( E \), instead of varying \( E \) for a given \( b \) as in the Ritz variational method. In other words, Eq. (5.6) can be shown to be a variational expression for \( b \).

The drawback of this (Fano-Lee) method is the necessity of iteration to determine \( b_\beta \) at each energy. However, the tedious iteration can be avoided by the following procedure. The trial function \( \Psi \) is represented in terms of a set of basis functions \( y_k \): \( \Psi = \sum_k c_k y_k \). These basis functions \( y_k \) need not be orthogonal, nor must they have any particular logarithmic derivative on the reaction zone surface. As a matter of fact, it is desirable for them to have a variety of boundary values. Inserting the above trial function into Eq. (5.6), the stationary condition for \( b \), i.e., \( \partial b / \partial c_k = 0 \), can then be applied to determine \( b_\beta \). This procedure amounts to solving the following generalized
eigenvalue system:

$$\Gamma \vec{c} = b \Lambda \vec{c}. \quad (5.7)$$

The matrices \( \Gamma \) and \( \Lambda \) are defined by

$$\Gamma_{kl} = \int_\Omega \left[ -\frac{1}{\mu N} \nabla_y^* \cdot \nabla_y y_l - \frac{1}{m_e} \nabla_r y_k^* \cdot \nabla_r y_l + 2y_k^* (E - V) y_l \right] d\omega$$

$$= 2 \int_\Omega y_k^* (E - H) y_l d\omega - \frac{1}{\mu N} \int_{\Sigma R} y_k^* \frac{\partial y_l}{\partial n} d\sigma_R - \frac{1}{m_e} \int_{\Sigma L} y_k^* \frac{\partial y_l}{\partial n} d\sigma_L, \quad (5.8)$$

$$\Lambda_{kl} = \int_{\Sigma R} y_k^* y_l d\sigma_R + \int_{\Sigma L} y_k^* y_l d\sigma_L. \quad (5.9)$$

It should be noticed that the eigensolutions of (5.7) are not orthogonal over the reaction zone volume. Instead they are orthogonal over the reaction zone surface, i.e., \( \int_\Sigma \Psi_\beta^* \Psi_\beta \sigma = 0 \), since \( \vec{c}_\beta \cdot \Lambda \vec{c}_\beta' = 0 \) for \( b_\beta \neq b_\beta' \). Thus they form a complete set which can be connected to asymptotic MQDT solutions at the reaction zone surface.

The number of nontrivial solutions to Eq. (5.7) should be determined on physical grounds. It should equal the number of open and weakly-closed fragmentation channels in which wavefunctions have nonvanishing amplitudes on the reaction zone surface.\[54\] A complete set of orthonormal surface harmonics \( \phi_i \) are thus introduced which are eigenfunctions of the Hamiltonian for all particles in the system except the escaping one. The \( \beta \)th \( R \)-matrix eigenvector is determined by projecting \( \phi_i \) onto \( \Psi_\beta \):

$$Z_{i\beta} = \int_\Sigma \phi_i^* \Psi_\beta d\sigma / N_\beta, \quad (5.10)$$

where the normalization constant is given by \( |N_\beta|^2 = \sum_i | \phi_i^* \Psi_\beta d\sigma |^2 \). The \( R \) matrix is finally given by the expression:

$$(R^{-1})_{i\beta'} = \sum_\beta Z_{i\beta} b_\beta (Z^{-1})_{\beta i'}. \quad (5.11)$$
It is seen that this form of the eigenchannel $R$-matrix method is first of all noniterative. The problem of determining logarithmic derivatives $b_\beta$ of the $R$-matrix eigenstates $\Psi_\beta$ at a given energy $E$ is reduced to solving the linear generalized eigensystem (5.7). Second, the fact that no constraint needs to be imposed on the variational basis functions $y_\mu$ permits flexibility in different applications. One may choose these functions on physical grounds. All short-range coupling of electronic and nuclear degrees of freedom is finally included in the $R$ matrix, which can be converted into a reaction matrix by connecting $\Psi_\beta$ to the long-range close-coupling-type solutions.

5.3 Unified treatment of molecular ionization and dissociation

We have applied the noniterative eigenchannel $R$-matrix method outlined in the previous section to describe the coupling of electronic and nuclear motion when both ionization and dissociation processes are present.

5.3.1 Variational basis functions We first concentrate on how to determine the variational basis functions within the reaction zone $r < r_2$, $R < R_0$. As we discussed earlier, the noniterative $R$-matrix method allows considerable flexibility to choose variational basis functions on the basis of convenience and/or physical grounds. In our problem, we want eventually to describe processes in which either an electron can escape into region $r > r_2$ (ionization) or else two nuclei can be separated to large internuclear distances $R > R_0$ (dissociation). We may accordingly choose two types of variational basis functions. Basis functions of the first type are required to vanish at $R_0$ while they have a variety of values at $r_2$. This basis set can thus be used to account efficiently for ionization processes. The second type of basis
functions, describing dissociation processes, are required to vanish at \( r_2 \), but have finite values at \( R_0 \).

Following Jungen's treatment,[17] the reaction zone is further divided into several sub-regions. The reason for doing this is as follows. In the usual MQDT treatment of ionization processes, the Born-Oppenheimer approximation is adopted throughout the reaction volume, while the large-r nonadiabatic effect is fully accounted for by a laboratory-frame close coupling expansion in the outer region. This procedure is well justified since the region where the Born-Oppenheimer separation is valid (typically less than 10\( a.u. \)) coincides roughly with the size of the molecular core. However, a molecule in an excited electronic state may occupy a much larger space. For instance, the \( D(3p\pi) \) state of \( H_2 \) predissociates through the \( B'(3p\sigma) \) and \( C(2p\pi) \) states. While the \( C \) state is well confined within a region \( r < 10a.u. \), the \( B' \) state extends beyond \( r = 20a.u. \). It is thus necessary to consider the breakdown of the Born-Oppenheimer approximation even within the reaction region in order to treat dissociations through those electronic states. This breakdown, however, is not severe in some cases, as in Robicheaux's treatment of dissociative attachment in \( H_2 \).[63]

The Born-Oppenheimer approximation is accordingly assumed only within the region \( r < r_1 \). Each of the variational basis functions in this region can be written as a Born-Oppenheimer product. In the outer region of the reaction zone \( r_1 < r < r_2 \), on the other hand, our basis functions should be written as a laboratory-frame multichannel expansion in order to account for the breakdown of the Born-Oppenheimer approximation. Following the procedures in previous chapters, we can generate basis functions in this region.
by a rovibrational frame transformation performed at \( r = r_1 \). For simplicity, we neglect the energy dependence of short-range parameters like \( \mu_{\lambda}(R) \) in our present formulation. This dependence can be included, if important, by following the procedure outlined in Chapter 4.

The first basis set (ionization type) is formed in terms of the complete set of target eigenstates \( \phi^{(1)}_{N+u^+} \) of target eigenstates \( \langle \varphi^{(e)}_{\lambda_o}(N)\chi^{(1)}_{N+u^+}(R)\Phi^{(N^*)}_{J_M} \rangle \):

\[
y_{N+u^+}(E) = \sum_{N+u^+} \phi^{(1)}_{N+u^+} [f^{(1)}_{N+u^+}(r)C_{N+u^+,N+u^+} - g^{(1)}_{N+u^+}(r)S_{N+u^+,N+u^+}].
\]

(5.12)

Here again we assume for simplicity that only a single outer electron partial wave (\( l \)) is present outside the core region. A complete set of rovibrational functions \( \chi^{(1)}_{N+u^+}(R) \) of the target (with energy \( E^{(1)}_{N+u^+} \)) are determined by requiring \( \chi^{(1)}_{N+u^+}(R_0) = 0 \) (so that the \( y_{N+u^+} \) all vanish at \( R = R_0 \)). The \( C \) and \( S \) matrices are obtained by a rovibrational frame transformation at \( r_1 \), as before. For example,

\[
C_{N+u^+,N+u^+} = \sum_{\lambda} U^{(J')}_{N+u^+} < \chi^{(1)}_{N+u^+}(R) | \cos \mu_{\lambda}(R) | \chi^{(1)}_{N+u^+}(R) > U^{(J')}_{N+u^+},
\]

(5.13)

with \( J' \) denoting the (final state) total angular momentum of the system. These functions (all at the same total scattering energy \( E \)) having various finite values at \( r = r_2 \) (but vanishing at \( R_0 \)) are primarily used to describe ionization of the molecule.

The second portion of the basis set (dissociation type), which will be used to describe predominantly dissociation processes, can be obtained by the following two steps. First a multichannel expansion like Eq. (5.12) can be formed in terms of a different complete set of target eigenstates \( \phi^{(2)}_{N+u^+} \)
The vibrational wavefunctions are determined by requiring \( \chi^{(2)}_{N^* u^*}(R_0) = 0 \) in this case (thus \( y^{(2)}_{N^* u^*}(E) \) have variety of values at \( R_0 \)). The matrix element \( C^{(2)}_{N^* u^*, N'^* u'^*} \) in the above formula has a similar expression to that of \( C^{(2)}_{N^* u^+, N'^* u'^+} \), except that it is evaluated with rovibrational wavefunctions \( \chi^{(2)}_{N^* u^+}(R) \). This set of basis functions (also all at the scattering energy \( E \)) would normally not vanish on the electronic part of the reaction surface (at \( r = r_2 \)). A second step, similar to the MQDT procedure of calculating bound energy levels, is followed to determine a discrete set of basis functions at energies \( E_d \). This can be accomplished by requiring that a linear combination of the above solutions in Eq. (5.14), namely \( y = \sum_{N^* u^*, N'^* u'^*} D_{N^* u^*, N'^* u'^*} y^{(2)}_{N^* u^*, N'^* u'^*} \), should vanish at \( r = r_2 \), i.e., by requiring

\[
\sum_{N^* u^*, N'^* u'^*} [f^{(2)}_{N^* u^+}(r_2)C^{(2)}_{N^* u^+, N'^* u'^*} - g^{(2)}_{N^* u^+}(r_2)S^{(2)}_{N^* u^+, N'^* u'^*}]D_{N^* u^*, N'^* u'^*} = 0. \quad (5.15)
\]

This condition will be satisfied only at certain energies \( E_d \). Thus we obtain the following basis set of the dissociation type,

\[
y_d(E_d) = \sum_{N^* u^+} \phi^{(2)}_{N^* u^+} [f^{(2)}_{N^* u^+}(r)C_{N^* u^+, d} - g^{(2)}_{N^* u^+}(r)S_{N^* u^+, d}]. \quad (5.16)
\]

Here

\[
C_{N^* u^+, d} = \sum_{N'^* u'^*} C^{(2)}_{N^* u^+, N'^* u'^*} D_{N'^* u'^*, d}, \quad (5.17)
\]

with \( D_{N'^* u'^*, d} \) being the superposition constant determined from \( y|_{r=r_2} = 0 \).
5.3.2 Variational R-matrix calculation  These two types of basis sets \( \{ y_k, k = N^+v^+, d \} \), having been obtained using a frame transformation, are now used as basis functions in a variational \( R \)-matrix calculation:

\[
\Psi = \sum_{N^+v^+} y_{N^+v^+} c_{N^+v^+} + \sum_d y_d c_d. \tag{5.18}
\]

Note that this basis set has been designed to generate the physically-correct number of eigensolutions to Eq. (5.7), namely the total number of open and weakly-closed ionization and dissociation channels. The \( \Gamma \) and \( \Lambda \) matrices used in Eq. (5.7) can be calculated using our variational basis functions. The \( \Lambda \) matrix involves integrals along the portions of the reaction surface, \( r = r_2 \) for the ionization part, and \( R = R_0 \) for the dissociation part. The portion of the matrix in the ionization basis is simply given by

\[
\Lambda_{N^+v^+, N'^+v'^+} = \sum_{N^+v^+} \left\{ \left( \begin{array}{c} f_N^{(1)}(r) C_{N^+v^+, N'^+v'^+} - g_N^{(1)}(r) S_{N^+v^+, N'^+v'^+} \\ f_N^{(1)}(r) C_{N^+v^+, N'^+v'^+} - g_N^{(1)}(r) S_{N^+v^+, N'^+v'^+} \end{array} \right) \right\}|_{r=r_2}. \tag{5.19}
\]

The elements coupling ionization channels and dissociation channels vanish in \( \Lambda \) since each basis function vanishes on one surface or the other, i.e.,

\[
\Lambda_{N^+v^+, d} = \Lambda_{d, N^+v^+} = 0. \tag{5.20}
\]

The portion of the \( \Lambda \) matrix in the dissociation basis, on the other hand, needs a little consideration. According to Eq. (5.9), these matrix elements involve integrations of all electronic coordinates from \( r = 0 \) to \( r = r_2 \) along the reaction surface \( R = R_0 \). Basis functions \( y_d \) are determined in the outer region of the reaction zone (\( r > r_1 \)). However, they will evolve into Born-Oppenheimer states in the region \( r < r_1 \). So the integrations can be carried
out from \( r = 0 \) to \( r = r_1 \) using the Born-Oppenheimer basis states and then from \( r = r_1 \) to \( r = r_2 \) using basis functions having the multichannel expansion form of Eq. (5.16). These integrations can be evaluated using the following identity:

\[
\int \phi_i \phi_j \, dx = \frac{1}{2} \left( \phi_i \frac{\partial \phi_j}{\partial x} - \phi_j \frac{\partial \phi_i}{\partial x} \right) \Bigg|_{x_1}^{x_2} / (\epsilon_i - \epsilon_j),
\]

where \( \phi_i \) and \( \phi_j \) are two eigensolutions of the same Hamiltonian with different eigenvalues \( \epsilon_i \) and \( \epsilon_j \), respectively. Since wavefunctions at \( r = 0 \) (Born-Oppenheimer states) vanish, the final result of integration can be determined through the values of \( \gamma_d \) at \( r_2 \),

\[
\Lambda_{dd'} = \sum \sum \chi_{N+v}^{(2)}(R_0) \chi_{N',v'}^{(2)}(R_0) \frac{(\varphi_{N+v,d} \varphi_{N'+v',d'}' - \varphi_{N'+v',d'} \varphi_{N+v,d})|_{r=r_2}}{2[(E_d - E_{N+v}^{(2)}) - (E_{d'} - E_{N'+v'}^{(2)})]},
\]

where \( \varphi_{N+v,d} = f_{N+v,d}^{(2)} S_{N+v,d} \) and \( \varphi_{N'+v',d'} \) denotes derivative of \( \varphi_{N+v,d} \) with respect to \( r \). According to Eq. (5.15), \( \varphi_{N+v,d} \) vanishes at \( r = r_2 \).

Consider \( \Lambda_{dd'} (d \neq d') \) first. In this case the energy denominator will not vanish generally, giving

\[
\Lambda_{dd'} = 0 \quad d \neq d'.
\]

For \( d = d' \), the same argument applies to the terms with \( v^+ \neq v'^+ \) in the summation. For the \( v^+ = v'^+ \) terms, on the other hand, both denominator and numerator vanish at the same time. We may expand terms with \( \{ N^+v'^+ \} \) about \( \{ N^+v^+ \} \) in the sense of a Taylor series, and take the limit \( v'^+ \to v^+ \). This gives rise to terms which are derivatives with respect to energy. After
some manipulation, we have

\[ \Lambda_{dd} = \sum_{N^* + v^+} \left[ \frac{x_{N^* + v^+}^{(2)}(R_0)}{2} \left\{ \left[ f_{N^* + v^+}^{(2)} \frac{\partial g_{N^* + v^+}^{(2)}}{\partial E} \right] (C_{N^* + v^+ + d})^2 + \right. \right. \\
\left. \left. \left[ g_{N^* + v^+}^{(2)} \frac{\partial f_{N^* + v^+}^{(2)}}{\partial E} \right] (S_{N^* + v^+ + d})^2 - \left[ f_{N^* + v^+}^{(2)} \frac{\partial g_{N^* + v^+}^{(2)}}{\partial E} \right] \right. \right. \\
\left. \left. \left[ g_{N^* + v^+}^{(2)} \frac{\partial f_{N^* + v^+}^{(2)}}{\partial E} \right] \right\} \right|_{r=r_2}. \] (5.24)

In the above formula, \( [f_{N^* + v^+}^{(2)}, \frac{\partial f_{N^* + v^+}^{(2)}}{\partial E}] \) denotes the wronskian of \( f_{N^* + v^+}^{(2)} \) and \( \frac{\partial f_{N^* + v^+}^{(2)}}{\partial E} \). The energy derivative of \( (f_{N^* + v^+}^{(2)}, g_{N^* + v^+}) \) at \( r_2 \) can be evaluated to a good approximation in the following way:

\[ \frac{\partial f_{N^* + v^+}^{(2)}}{\partial E} \approx \frac{f_{N^* + v^+ + 1}^{(2)} - f_{N^* + v^+ - 1}^{(2)}}{E_{N^* + v^+ + 1} - E_{N^* + v^+ - 1}} \] (5.25)

since the rovibrational energy spacing is rather small.

The \( \Gamma \) matrix elements include both volume and surface integrals. For those elements involving ionization channels, the volume integrals vanish since our ionization basis states are eigenstates of Hamiltonian at total energy \( E \), to within the accuracy of the frame transformation. These elements are given by

\[ \Gamma_{N^* + v^+, N' + v^+'} = -\sum_{N^* + v^+} \left\{ (f_{N^* + g^+}^{(1)} C_{N^* + g^+, N^* + v^+} - g_{N^* + g^+, N^* + v^+}^{(1)} S_{N^* + g^+, N^* + v^+}) \times \\
(f_{N^* + g^+}^{(1)'})' C_{N^* + g^+, N' + v^+'} - g_{N^* + g^+, N' + v^+'}^{(1)'}) S_{N^* + g^+, N' + v^+'} \right\} \right|_{r=r_2}, \] (5.26)

\[ \Gamma_{N^* + v^+, d} = \frac{1}{2\mu N} \sum_{N^* + g^+, N^* + v^+} \sum_{N^* + g^+, N^* + v^+} \frac{\chi_{N^* + g^+}^{(1)'}}{(E - E_d)} \left( f_{N^* + g^+, N^* + v^+}^{(1)} C_{N^* + g^+, N^* + v^+} - g_{N^* + g^+, N^* + v^+}^{(1)} S_{N^* + g^+, N^* + v^+} \right) \times \\
\left( f_{N^* + g^+, N^* + v^+, d}^{(2)} - g_{N^* + g^+, N^* + v^+, d}^{(2)} S_{N^* + g^+, N^* + v^+, d} \right) \right|_{r=r_2}. \] (5.27)
For the dissociative part of the $T$ matrix, volume integrals are involved. However, following the same spirit of the treatment using Eq. (5.21), those volume integrals can be reduced to surface integrals. We finally have

$$
\Gamma_{dd'} = 0 \quad d \neq d',
$$

(5.28)

$$
\Gamma_{dd} = -(E - E_d) \sum_{N+u+} \left\{ \left[ f_{N+u+}^{(2)}(E), \frac{\partial f_{N+u+}^{(2)}(E)}{\partial E} \right] (C_{N+u+})^2 + \left[ g_{N+u+}^{(2)}(E), \frac{\partial g_{N+u+}^{(2)}(E)}{\partial E} \right] (S_{N+u+})^2 - \left( f_{N+u+}^{(2)}(E), \frac{\partial g_{N+u+}^{(2)}(E)}{\partial E} \right) \right\} \left|_{r=r_2} \right.
$$

(5.29)

It is seen that the pure ionization part of the $T$ matrix exhibits a slight asymmetry owing to the assumption that the basis functions are eigenfunctions of the Hamiltonian. Hence a symmetrized matrix \([\Gamma_{N+u+ \to N+u+'}, \Gamma_{N+u+' \to N+u+})/2\), for instance] is used in the calculation, which is permissible since the asymmetry in practice is of order $10^{-3}$, i.e., relatively small.

In order to obtain the $R$-matrix eigenvectors, we need to project our $R$-matrix eigenstates $\Psi_\beta$ onto the following surface harmonics

$$
\phi_{N+u+} = \varphi^{(r)}_{\Lambda} (N) \chi^{(1)}_{N+u+} (R) \Phi^{(N+)}_{fM} \quad r = r_2 \quad \text{(ionization channels)},
$$

$$
\phi_{\Lambda} = \varphi^{(r)}_{\Lambda} (N + 1) \mathcal{D}_{\Lambda M} \quad R = R_0 \quad \text{(dissociation channels)}.
$$

Here we assume one dissociation channel for each $\Lambda$. It is straightforward to extend the treatment to include more channels. The projection coefficients on the $r = r_2$ surface are given as follows:

$$
a_{N+u+' \to N+u+} = \int \phi^{(1)}_{N+u+'}(r_2) y_{N+u+} \cdot d\sigma_r
$$

$$
= f_{N+u+}^{(1)}(r_2) C_{N+u+' \to N+u+'}, - g_{N+u+}^{(1)}(r_2) S_{N+u+ \to N+u+'},
$$

(5.30)
Projection of a dissociative basis function $y_d$ onto the surface harmonics on $R = R_0$ surface has not yet been fully understood. We assume at this stage that $y_d$ is nearly a Born-Oppenheimer state of $\Lambda$ character on surface $R = R_0$, and use

$$a_{\Lambda,d} = \int \phi_{\Lambda}^* y_d d\sigma_R$$

$$= \sqrt{\Lambda_{dd}}, \quad (5.31)$$

since $\Lambda_{dd}$, by definition, can also be evaluated as $\sum_\Lambda a_{\Lambda,d}^2$, using the surface harmonics $\phi_{\Lambda}$ in the integration Eq. (5.9). The eigenvectors of the $R$ matrix can finally be formed according to Eq. (5.10)

$$Z_{N^+,v^+} = \sum_{N^+,v^+} a_{N^+,v^+} Z_{N^+,v^+}, \quad (5.32)$$

$$Z_{\Lambda,\beta} = \sum_d a_{\Lambda,d} c_{d,\beta} / N_\beta. \quad (5.33)$$

5.3.3 MQDT calculations

The variational $R$-matrix calculation [Eq. (5.7)] gives a complete set of eigenstates $\Psi_\beta$ which are orthogonal over the reaction zone surface, having logarithmic derivatives $b_\beta(E)$:

$$\Psi_\beta|_{r=r_2} = \sum_{N^+,v^+} \phi_{N^+,v^+} Z_{N^+,v^+}, \quad (5.34)$$

$$\Psi_\beta|_{R=R_0} = \sum_\Lambda \phi_{\Lambda} Z_{\Lambda,\beta}. \quad (5.35)$$

Each linearly-independent eigensolution in the asymptotic region can be written as

$$\Psi_\beta|_{r>r_2} = \sum_{N^+,v^+} \phi_{N^+,v^+} f^{(1)}_{N^+,v^+}(r) I_{N^+,v^+,\beta} - g^{(1)}_{N^+,v^+}(r) J_{N^+,v^+,\beta}, \quad (5.36)$$

$$\Psi_\beta|_{R>R_0} = \sum_\Lambda \phi_{\Lambda} [F_\Lambda(R) I_{\Lambda,\beta} - G_\Lambda(R) J_{\Lambda,\beta}], \quad (5.37)$$

where $(F_\Lambda, G_\Lambda)$ are regular and irregular (energy-normalized) nuclear vibrational wavefunctions calculated in the potentials of the dissociative electronic
states. The $I$ and $J$ matrices, which play the same role as the reaction matrix, can thus be determined by matching the outer region solutions to the inner region $R$-matrix eigenstates on the reaction zone surface:

$$I_{N+u+,\beta} = \left[ g_{N+u+}^{(1)}(r_2) + g_{N+u+}^{(1)}(r_2) b_{\beta} \right] Z_{N+u+,\beta}, \quad (5.38)$$

$$J_{N+u+,\beta} = \left[ f_{N+u+}^{(1)}(r_2) + f_{N+u+}^{(1)}(r_2) b_{\beta} \right] Z_{N+u+,\beta}, \quad (5.39)$$

$$I_{A,\beta} = \left[ G_A'(R_0)/\mu_N + G_A(R_0) b_{\beta} \right] Z_{A,\beta}, \quad (5.40)$$

$$J_{A,\beta} = \left[ F_A'(R_0)/\mu_N + F_A(R_0) b_{\beta} \right] Z_{A,\beta}. \quad (5.41)$$

At this stage, the physical boundary conditions in the asymptotic regions have not been applied. Following the same procedures of Chapter 2, the physically-correct wavefunctions can be formed by superposing all independent eigensolutions $\Psi_{\beta}$ in the asymptotic region [Eqs. (5.36) and (5.37)] and imposing appropriate boundary conditions both at large electronic distance (ionization channels) and large internuclear distance (dissociation channels). The final "collision eigenchannel" solutions in the asymptotic regions can be written as

$$\Psi_{\rho} = \sum_{N+u+ \in P} \phi_{N+u+} T_{N+u+,\beta} [f_{N+u+}(r) \cos \delta_{\rho} - g_{N+u+}(r) \sin \delta_{\rho}] \quad r > r_2 \quad (5.42)$$

$$\Psi_{\rho} = \sum_{A \in P} \phi_A T_{A,\beta} [F_A(R) \cos \delta_{\rho} - G_A(R) \sin \delta_{\rho}] \quad R > R_0. \quad (5.43)$$

where $\delta_{\rho}$ and $T$ are eigenvalues and eigenvector matrix of the full scattering matrix including both ionization and dissociation channels. $P$ refers to the open channels.

Positions and widths of predissociation and preionization levels are determined from the eigenphase sum $\delta_{\text{sum}} = (1/\pi) \sum_{\rho} \delta_{\rho}$ which shows a Breit-Wigner profile near the resonance levels.
The photoionization oscillator strength (from the ground electronic state of $H_2$ to a final state with $H^+_2$ left in the rovibrational state $\{N^+v^+\}$) is given in atomic units by

$$\left. \frac{df}{dE} \right|_{N^+v^+} = \frac{2\hbar\nu}{2J'' + 1} \sum_{M''} |D_{N^+v^+}^{J''M''}|^2,$$

(5.44)

where $D_{N^+v^+}^{J''M''}$ is the electric dipole moment which is defined by

$$D_{N^+v^+}^{J''M''} = \langle \Psi_{N^+v^+}^{(-)} | \hat{r} | \Psi_0 \rangle,$$

(5.45)

and $\Psi_0$ denotes the ground electronic state of $H_2$ in a rovibrational state $\{J'' = 0; v''\}$, and $\Psi_{N^+v^+}^{(-)}$ denotes the final state of the system (obeying the incoming wave boundary condition[22,16] — leading to an outgoing $p$-wave photoelectron plus an $H^+_2$ core in its rovibrational state $\{J' = 1; N^+ = 0, 2; v^+\}$). If $J'' \neq 0$, then one needs to sum over the final state $J'$ and $M'$ in Eq. (5.44).

In order to evaluate the dipole transition matrix element, we follow the same procedures as Ref. [16]. Photoabsorption from the ground state takes place initially in a small region of space where the Born-Oppenheimer approximation is valid. We can reexpand the final wavefunctions $\Psi_{N^+v^+}$ in terms of the Born-Oppenheimer wavefunctions which are more relevant at short-range, as follows. The dipole transition matrix element can first be written in terms of a “collision eigenchannel” dipole matrix element $D_\rho$. Then $D_\rho$ is decomposed in terms of $R$-matrix eigenstates $\Psi_\beta$. The $R$-matrix eigenstates are each a sum of the variational basis functions which finally can be expressed at $r < r_1$ in terms of Born-Oppenheimer states. This procedure can be explicitly written as follows:

$$D_{N^+v^+}^{J''M''} = \sum_\rho \exp(i\delta_\rho) T_{N^+v^+\rho} D_\rho,$$

(5.46)
and
\[ D_\rho = \langle \Psi_\rho | \hat{\varepsilon} \cdot \hat{r} | \Psi_0 \rangle = \sum_\beta A_{\beta \rho} < \Psi_\beta | \hat{\varepsilon} \cdot \hat{r} | \Psi_0 > \]
\[ = \sum_\beta A_{\beta \rho} \left( \sum_{N^+} c_{N^+ N^+ \beta} < y_{N^+ | \hat{\varepsilon} \cdot \hat{r} | \Psi_0 > + \sum_d c_{d \beta} < y_d | \hat{\varepsilon} \cdot \hat{r} | \Psi_0 > \right), \]
(5.47)

Both \( y_{N^+ \sigma^+} \) and \( y_d \) are superpositions of Born-Oppenheimer states, i.e., a mixture of states with different \( \Lambda \)'s. The ground state of \( H_2 \) can be written as a Born-Oppenheimer product in the same way. Electronic transitions are much faster processes than those of nuclei. The Franck-Condon principle can be applied when evaluating the dipole moment \( d_\Lambda (R) \) of electronic transitions at fixed nuclear positions. We have the following results:
\[ < y_{N^+ \sigma^+} | \hat{\varepsilon} \cdot \hat{r} | \Psi_0 > = \sum_\Lambda U_{N^+ \sigma, \Lambda} < \chi_{N^+ \sigma, \Lambda} (R) | d_\Lambda (R) | \chi_{J'' \nu''} (R) > U_{J'' \nu'' \Lambda} \]
\[ \times (J'M''|J''M'', 10), \]
(5.48)

where \( \chi_{J'' \nu''} (R) \) is the vibrational wavefunction of \( H_2 \), \( U_{N^+ \sigma, \Lambda} \) is the rotational frame transformation factor which transforms the angular coupling scheme relevant in the body-frame (Hund's case \( b \)) to that relevant in the laboratory-frame (Hund's case \( d \)), as before. The product of the Clebsch-Gordan coefficient \( (J'M''|J''M'', 10) \) and the transformation coefficient \( U_{J'' \nu'' \Lambda} \) arise from the integrations over the nuclear angular coordinates with \( U_{J'' \nu'' \Lambda} \) given by the same expression as the rotational frame transformation factor (with \( l = 1 \) now representing the multipolarity of the dipole operator). When averaging over the initial magnetic sublevels, we obtain
\[ \frac{1}{2J'' + 1} \sum_{M''} |(J'M''|J''M'', 10)|^2 = \frac{1}{3 (2J'' + 1)}. \]
(5.49)
Writing \( D_\rho = (J'M''|J''M'',10)\bar{D}_\rho \), we have

\[
\bar{D}_\rho = \sum_\beta A_{\beta\rho} \left\{ \sum_{N^+6^+} c_{N^+6^+\beta} \sum_\Lambda U_{N^+\Lambda}^{J'} \chi_{N^+\Lambda}^{(1)}(R) |d_\Lambda(R)\chi_{J''\nu''}(R) > U_{J''\Lambda}^{J'} \right. \\
+ \left. \sum_d c_{d\beta} \sum_{N^+6^+} D_{N^+6^+d} \sum_\Lambda U_{N^+\Lambda}^{J'} \chi_{N^+\Lambda}^{(2)}(R) |d_\Lambda(R)\chi_{J''\nu''}(R) > U_{J''\Lambda}^{J'} \right\} 
\]

(5.50)

We finally obtain the following expression of the photoionization oscillator strength:

\[
\frac{df}{dE}_{N^+\nu^+} = \frac{2\hbar \nu}{3} \left( \frac{2J' + 1}{2J'' + 1} \right) \left| \sum_\rho \exp(i\delta_\rho) T_{N^+\nu^+\rho} \bar{D}_\rho \right|^2 
\]

(5.51)

To describe photoabsorption processes, we need to know \( d_\Lambda(R) \) in addition to \( \mu_\Lambda(R) \). All the fundamental information about the photoabsorption process ultimately is expressed in terms of these two quantities. Like \( \mu_\Lambda(R) \), \( d_\Lambda(R) \) can be obtained either from an \textit{ab initio} calculation, or else by fitting to experimental data.

### 5.3.4 Discussion

We have formulated this non-iterative \( R \)-matrix treatment in the same spirit as Jungen’s method.[17] The advantage of our treatment is that the iteration procedure is bypassed. This should make numerical calculations faster, although the derivation itself seems more complicated. However, because our variational basis functions for ionizations are energy dependent (they are all at the total scattering energy \( E \)), the \( \Gamma \) matrix for the generalized eigenvalue problem problem Eqs. (5.26) and (5.27) must be calculated at each scattering energy (since the Coulomb functions need to be calculated at each energy). This may become time-consuming in some applications. This problem may be simplified if an energy-independent basis
functions are used. In his treatment of $\text{H}_2$ vibrational excitations and dissociative attachment by electron collision, Robicheaux formulated an $R$-matrix method using a modified Greene-Jungen method. He was able to identify a set of energy-independent variational basis to simplify the calculation.[63] The disadvantage of his treatment, however, is that the Born-Oppenheimer approximation is assumed throughout the reaction region. This assumption breaks down in some applications, such as $\text{H}_2$ predissociation, as we mentioned earlier. The basis set adopted by Robicheaux is also apparently susceptible to linear dependence difficulties.

Like Jungen’s and Robicheaux’s treatments, the dissociation process at large $R$ is assumed here to be along well-defined Born-Oppenheimer states, i.e., we assume that all non-Born-Oppenheimer effects causing the dissociation process are confined to within a small $R$ region. This is certainly a good approximation for a dissociation which proceeds relatively slowly. If the nuclear recoil velocity is large, non-Born-Oppenheimer effects could arise at large $R$, of the type familiar in the context of electron translation factors.

As we stated, this formulation is a first step to understand the short-range coupling of electronic and nuclear degrees of freedom. There are still many things we do not understand. For instance, we have not yet fully understood the relation between our dissociative basis functions in the reaction zone and the Born-Oppenheimer dissociative electronic states at large $R$. This causes some difficulties and ambiguity in how to match the two solutions on the reaction zone surface $R = R_0$, as we mentioned in Sec. 5.3.2. Further study will be required to fully understand the physics involved in these processes.
5.4 Test calculations

In order to see how well this method can be applied to describe the processes of ionization and dissociation, we have carried out the following two test calculations: (1) predissociation of the \( D(3p\pi) J'' = 2, \nu = 3 \) level of \( \text{H}_2 \), which is below the ionization threshold and slightly above the dissociation limit \( \text{H}(1s) + \text{H}(2l) \); and (2) ionization spectra between the \( N^+ = 0 \) and \( N^+ = 2 \) of \( \text{H}_3^+ (J' = 1) \) thresholds. We then compare our results with other theoretical calculations. In these test calculations, we use for simplicity an infinite nuclear mass in calculating the electron reduced mass, which is needed in finding the effective quantum number in the asymptotic region. This appears to have little effect on the final results.

5.4.1 Predissociation of \( \text{H}_2 \) in the D state All energy levels above \( \nu = 2 \) in the \( D(3p\pi^1 \Pi_u^+ \) state of \( \text{H}_2 \) lie above the \( n = 2 \) dissociation limit. It has been known for some time that predissociation of these levels is induced by a transition into the \( B' (3p\sigma^1 \Sigma_u^+) \) vibrational continuum, caused by rotational (Coriolis) interaction. The interaction of the \( D \) state with \( C (2p\pi^1 \Pi_u^+) \) and \( B (2p\sigma^1 \Sigma_u^+) \) states is much weaker by orders of magnitude. The reason is that all coupling occurs at short internuclear distances, since in the united atom limit, the \( D \) and \( B' \) states approach the same electronic configuration \( \text{He}(3p) \). In other words, the \( D \) and \( B' \) potential curves are so close to each other at short internuclear distance that they can interact very effectively.[66] On the other hand, the \( C \) and \( B \) states are so far apart that their interaction with the \( D \) state is weak. The coupling to the \( 2p\pi \) state is about two orders of magnitude weaker than the coupling to \( 3p\sigma \) while
the coupling to $2p\sigma$ is even weaker and is thus neglected entirely in this calculation.

In order to describe the dissociation process correctly, we choose two dissociative basis functions characterizing these two dissociative states; each corresponds to one symmetry. In Fig. 24, we show the probability amplitude (averaged over angles) of the two dissociation-type basis functions (which are determined at energies $E_1 = 119951.1 \text{cm}^{-1}$ and $E_2 = 119515.5 \text{cm}^{-1}$) used in this calculation. It is seen by inspection that $y_1$ is basically a $3p\sigma$ electronic state in the "box" vibrational level $v = 6$ (one node in $r$ and six nodes in $R$ within $R < R_0$), while $y_2$ is the $2p\pi$ electronic state in the "box" vibrational level $v = 10$ (no nodes in $r$ and ten nodes in $R$). In Fig. 25, we show the corresponding contour plots of these two dissociation-type basis functions. These plots show also that the Born-Oppenheimer approximation is quite reasonable for these states, as a first approximation.

It is also seen that the $C$ state is well confined to within about 10 a.u. in the electronic coordinate $r$, while the $B'$ state extends to about 20 a.u. in $r$. It is crucial to have the $R$-matrix box large enough to hold the $3p\sigma$ state in $r$ since it is this state that strongly couples to the $3p\pi$ state. On the other hand, the $R$-matrix box should also be large enough in $R$ to include the Born-Oppenheimer $D(J'' = 2, v = 3)$ level. Our $R$-matrix box is chosen to have the dimensions $r_2 = 25 \text{a.u.}$, $R_0 = 4 \text{a.u.}$ Fifteen $H_2^+$ vibrational wavefunctions for each $N^+ (= 1, 3)$ are included in the calculation in addition to the two dissociative basis functions discussed above. In order to describe a dissociative basis function like $y_2$ in Fig. 24 ($v = 10$ state), we need at least 10—15 vibrational levels of the target.
Figure 24. Variational basis functions used in the calculation of $H_2$ predissociation. (a) Basis of $\Sigma$ character. (b) Basis of $\Pi$ character.
Figure 25. Contour plots of the corresponding dissociation-type basis functions in Fig. 24.
Figure 26. Eigenphase sum and its derivative with respect to energy are shown for the $D (3p\pi, J' = 2, v = 3)$ level of H$_2$. 
Figure 26 shows the eigenphase sum and its derivative with respect to energy as functions of energy near the position of $D(J = 2, v = 3)$. In this range of energy, all ionization channels are closed. The resulting Breit-Wigner-type profile arises almost totally from the predissociation to the $3p\sigma$ continuum state. It is seen from the reaction matrix that the coupling to the $2p\pi$ state is weaker by two orders of magnitude. The position $E_{cal} = 119319.0 \text{ cm}^{-1}$ and the width $\Gamma_{cal} = 14.9 \text{ cm}^{-1}$ of the level are reproduced in good agreement with the experiment $E_{exp} = 119318.3 \text{ cm}^{-1}, \Gamma_{exp} = 14.5 \pm 0.5 \text{ cm}^{-1}$ and previous theoretical calculations.\cite{14}

5.4.2 Photoionization spectra above dissociation limit

The second test calculation has treated photoionization spectra of para-hydrogen. At low temperature, para-hydrogen is populated only in the $J'' = 0$ state. Photoabsorption brings the system to the $J' = 1$ state. Since the photoelectron is mainly in a $p$ state, the rotational quantum numbers for the remaining $\text{H}_2^+$ can only have the values $N^+ = 1, 3$, by angular momentum conservation.

Following Ref. \cite{16}, we approximate the body-frame dipole operator $d_A(R)$ by the $R$-independent constant,

$$d_\Sigma = d_\Pi = d_0 = 1.86 \text{ a.u.}, \quad (5.52)$$

since at small-$R$ $d_\Sigma(R)$ and $d_\Pi(R)$ approach the same united atom limiting values. Using the above approximation, Eq. (5.50) becomes

$$\tilde{D}_\rho = d_0 V_\rho, \quad (5.53)$$
where
\[ V_\phi = \sum_\phi \sum_{\mu_{d,\phi}} \left\{ \sum_{\mu_{d,\phi}} c_{\mu_{d,\phi}} \langle \chi_{\mu_{d,\phi}}^{(1)} | \chi_{\mu_{d,\phi}}^{(2)} \rangle + \sum_{\mu_{d,\phi}} c_{\mu_{d,\phi}} D_{\mu_{d,\phi}} \langle \chi_{\mu_{d,\phi}}^{(1)} | \chi_{\mu_{d,\phi}}^{(2)} \rangle \right\}. \tag{5.54} \]

The total photoionization oscillator strength is given by a sum over the open ionization channels,
\[ \frac{df}{dE_{\text{ion}}} = \frac{2h\nu}{3} \frac{2J' + 1}{2J'' + 1} d_0^2 \sum_{N \nu} \{ (\sum_\rho \cos \delta_\rho T_{N \nu \rho} V_{\rho})^2 + (\sum_\rho \sin \delta_\rho T_{N \nu \rho} V_{\rho})^2 \}. \tag{5.55} \]

Similarly, the total photodissociation oscillator strength is given by
\[ \frac{df}{dE_{\text{diss}}} = \frac{2h\nu}{3} \frac{2J' + 1}{2J'' + 1} d_0^2 \sum_{A} \{ (\sum_\rho \cos \delta_\rho T_{A \rho} V_{\rho})^2 + (\sum_\rho \sin \delta_\rho T_{A \rho} V_{\rho})^2 \}, \tag{5.56} \]
and the total photoabsorption oscillator strength is the sum of the above two expressions.

We have calculated photoionization spectra between the \( N^+ = 0 \) and \( N^+ = 2 \) thresholds. Fig. 27 compares our photoionization oscillator strength calculation with that of Jungen and Dill, showing reasonably good agreement. The latter is a pure photoionization calculation, neglecting the dissociation channels altogether. In Fig. 28, we show our calculated dissociation spectra, for which there are no other experimental or theoretical results that can be compared. Note that photoionization dominates almost totally. All the fine structures are higher rovibrational states belonging to Rydberg electronic states. The Rydberg series converging to the \( \nu^+ = 0, N^+ = 2 \) threshold couples to the continuum of the Rydberg series converging to lower threshold \( \nu^+ = 0, N^+ = 0 \), giving rise to very rapid energy transfer from rovibrational degrees of freedom to electronic ones, at least on the time scale of the Rydberg electron motion.
Figure 27. Photoionization spectra of H$_2$. Left: Results of Jungen and Dill[16], (a) photoionization ionization spectra including rovibrational au­toionization and (b) direct ionization spectra; Right: Results of present cal­culation, ionization spectra (solid line) and total photoabsorption spectra (dotted line).
It will be more interesting to calculate photoabsorption spectra in regions where dissociation and ionization compete with each other more comparably. This will give a crucial test of our method. Further calculations will be needed to ascertain the accuracy of this treatment in such spectral regions.
CHAPTER 6

CONCLUSIONS

We have demonstrated in this dissertation how the multichannel quantum defect theory, combined with a frame transformation, can be used to describe three important non-adiabatic effects in electron scattering from a homonuclear diatomic molecule, i.e., the effects arising from large electron molecule distances, from resonances, and those responsible for dissociation processes. Complicated coupling between electronic and nuclear degrees of freedom has been shown to be mainly confined within a small region of space around the molecular target. Unlike the usual "adiabatic nuclei approximation", the Born-Oppenheimer approximation is assumed only within this region. MQDT enables us to single out a few scattering parameters, like the body-frame quantum defect function, $\mu_A(\epsilon, R)$, for instance, to characterize this short-range interaction. With the help of a frame transformation, this function governs the evolution of the wavefunction of the whole system into asymptotic regions where experimental observables can be extracted.

For non-resonant scattering, the electron is able to cross the molecular target in a period of time much shorter than a nuclear rotational or vibrational periods. The target can thus be assumed to be frozen during scattering. An energy-independent frame transformation is shown to be (usually) accurate enough to describe the rovibrational coupling resulting from the $\Lambda$ and $R$ dependences of the quantum defect function (like in our calculations
of \( \text{H}_2^+ \) vibrational energy levels, and of the competing ionization and dissociation processes in \( \text{H}_2 \). However, when the collision time of the outermost electron becomes comparable to the time for nuclear rovibrations, an energy-dependent frame transformation should be used to account for the "dynamic" coupling of the electron to the target when the electron is close to the core. We have shown that the energy dependence of the quantum defect function is primarily responsible for this non-adiabatic effect. Our energy-dependent rovibrational frame transformation method, without invoking any electron-molecule compound states, is able to describe this class of non-adiabatic effects resulting from non-negligible time delay of the scattering electron in rovibrational excitation processes. This was illustrated by our calculations of the vibrational excitation of \( \text{H}_2 \) and \( \text{N}_2 \) by electron collision.

As we mentioned in chapter 5, a dissociative process is the most basic, prototype reactive process in a molecular system. The resulting competition between ionization and dissociation processes is of fundamental theoretical and experimental interest. Understanding how short-range electronic and nuclear coupling mediate the decay of the system into such different escape channels is a very general problem which needs to be better understood for other few-body system. This is the goal of our future work.

We have concentrated on the study of rovibrational couplings in this work. Processes involving electronic couplings have not yet been sufficiently well understood in our energy-dependent frame transformation method (chapter 4) nor in our preliminary treatment of ionization and dissociation (chapter 5). Without treating the energy dependence of the quantum defect, the electronic coupling has been studied, within the content of MQDT, by Raseev,[56]
Ross and Jungen,[57] Giusti-Suzor and Lefebvre-Brion,[67], and Giusti-Suzor and Jungen.[19] In Giusti-Suzor’s treatment, the rovibrational frame transformation described in chapter 2 is still used to describe the rovibrational coupling. In addition to the quantum defect function, a second body-frame interaction parameter is needed to account for the electronic coupling between electronic states in a perturbative way. This treatment has been successfully applied to describe dissociative recombination processes for several molecules (H₂, O₂, and NO, etc)[19, 20, 67] where electronic coupling is weak. We will continue to study this class of couplings in the future in order to fully understand the short-range coupling between electronic and nuclear motion, and eventually to treat those processes as well.
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VITA

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